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DEPARTMENT OF
HEALTH AND ENVIRONMENTAL SCIENCES
Natural Resource Damage Program
(406) 443-6103

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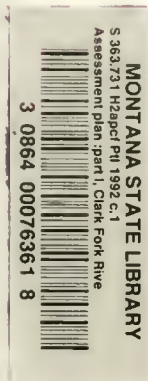
MEMORANDUM

TO: Libraries

FROM: Dick Pedersen, Manager *Dick Pedersen*

DATE: January 27, 1992

SUBJECT: Notice of Assessment Plan Part I



Attached are four (4) copies of Part I of the Assessment Plan for the Clark Fork River Basin NPL Sites, Montana. The Natural Resource Damage Program will be releasing this plan shortly by select mailings and issuance of a news release. Your library will be able to assist the general public by having this plan available for viewing and commenting.

DJP/asw

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DEPARTMENT OF
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STATE OF MONTANA

FAX # (406) 444-2806

NOTICE OF ASSESSMENT PLAN

HELENA, MONTANA 59620

The State of Montana, acting on behalf of the people of Montana, as trustee of the natural resources in the state, hereby provides notice pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act ("CERCLA"), 42 U.S.C. §§ 9601-9675, the U.S. Department of the Interior ("DOI") Natural Resource Damage Assessments ("NRDA") Regulations, 43 C.F.R. Part 11, and the Montana Comprehensive Environmental Cleanup and Responsibility Act ("CECRA"), Mont. Code Ann. §§ 75-10-701 to 75-10-724.

1. The Atlantic Richfield Company ("ARCO") has been identified by the State of Montana as the primary responsible party for facilities located at the Clark Fork River Basin National Priorities List ("NPL") sites, including the Silver Bow Creek/Butte Area site, the Anaconda Smelter site, the Montana Pole site, and the Milltown Reservoir site. There have been multiple and at times continuous releases of hazardous substances, including but not limited to arsenic, beryllium, cadmium, copper, creosote, lead, pentachlorophenol ("PCP"), polycyclic aromatic hydrocarbons, selenium, silver, volatile organic compounds, and zinc, from these facilities. Potential injuries to natural resources, including surface water, fish, sediments, ground water, air, soil, vegetation and wildlife, have resulted from these releases.

2. On October 10, 1991, the State of Montana issued its Notice of Intent to Perform an Assessment ("Notice") and released its Preassessment Screen: Clark Fork River Basin NPL Sites, Montana ("Preassessment Screen"). The Notice and Preassessment Screen were provided to ARCO, other interested parties, and members of the public. In accordance with the DOI NRDA regulations, Montana invited ARCO to participate in the development of a natural resource damage assessment and in the performance of the assessment. If ARCO wished to participate in the assessment, it was requested to provide to the State of Montana a damage assessment plan pursuant to the DOI NRDA regulations. ARCO subsequently submitted written comments to the State of Montana regarding the Preassessment Screen and the State's decision to perform a natural resource damage assessment. ARCO did not submit an assessment plan, nor did it indicate any intention to do so in the future. The State reviewed and considered the comments provided by ARCO in its preparation of this Assessment Plan.

3. The State of Montana hereby releases its Assessment Plan, Part I, Clark Fork River Basin NPL Sites, Montana ("Part I of the Assessment Plan"). This assessment plan identifies the methodologies for conducting injury determination and quantification for the surface water, fisheries, sediments, and groundwater resources. Part I of the Assessment Plan is being made

available for review and comment by ARCO, other natural resource trustees, other affected federal or state agencies or Indian tribes, and any other interested members of the public for a period of 30 calendar days. Comments concerning the assessment plan should be made in writing and sent by March 2, 1992, to:

Dick Pedersen
Natural Resource Damage Program Manager
Environmental Sciences Division
Department of Health and Environmental Sciences
Cogswell Building
Helena, MT 59620

The State of Montana may modify Part I of the Assessment Plan following its review of submitted comments. Any modifications, which in the judgment of the State of Montana are significant, will be made available for subsequent review and comment.

4. The State of Montana intends to release Part II of the Assessment Plan in the spring of 1992. Part II of the Assessment Plan will identify the methodologies for conducting injury determination and quantification for the air, soil, vegetation, and wildlife resources. It will also contain a preliminary determination of recovery periods for the injured resources, as well as the methodologies for assessing economic damages. Part II of the Assessment Plan will be made available for another 30-day review and comment period.

5. At the conclusion of the Natural Resource Damage Assessment, the State of Montana will prepare and make available a Report of the Assessment. The report will contain a summary of the comments received to Parts I and II of the Assessment Plan and the State's responses to those comments.

DATED this 27 day of January, 1992.

STATE OF MONTANA

By Dick Pedersen
Dick Pedersen
Natural Resource Damage Program
Manager
Environmental Sciences Division
Department of Health and
Environmental Sciences
Cogswell Building
Helena, MT 59620

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**ASSESSMENT PLAN:
PART I
CLARK FORK RIVER BASIN NPL SITES,
MONTANA**

**STATE OF MONTANA
NATURAL RESOURCE DAMAGE PROGRAM**

JANUARY 1992

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EXECUTIVE SUMMARY

The State of Montana ("the State") has commenced an action against the Atlantic Richfield Company ("ARCO") in the United States District Court for the District of Montana (Civil Action No. CV 83-317-HLN-CCL) pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act ("CERCLA"), 42 U.S.C. §§ 9601-9675, and the Montana Comprehensive Environmental Cleanup and Responsibility Act ("CECRA"), Mont. Code Ann. §§ 75-10-701 to 75-10-724. In this action, Montana seeks to recover damages for injuries to natural resources resulting from releases of hazardous and/or deleterious substances from facilities for which ARCO is the primary responsible party. The State of Montana has begun to assess the natural resource damages in accordance with the regulations of the U.S. Department of the Interior (DOI) as set forth in 43 CFR Part 11.

The purpose of this Assessment Plan is to ensure that the assessment is performed in a planned and systematic manner. The Assessment Plan identifies those scientific and economic methodologies that are expected to be performed in the assessment.

Part I of the Assessment Plan addresses activities associated with injury determination and quantification phases for four potentially injured natural resources: surface water resources, fisheries resources, sediment resources, and groundwater resources. Part II of the Assessment Plan, which will be completed and made available in the spring of 1992, will contain methodologies for conducting injury determination and quantification for soil resources, vegetation resources, wildlife resources, and air resources, a preliminary determination of recovery periods for potentially injured resources, as well as methodologies for assessing economic damages.

Part I of the Assessment Plan describes coordination of the assessment with investigations conducted pursuant to the Remedial Investigation/Feasibility Study (RI/FS) process currently underway at the four NPL sites in the Clark Fork Basin, procedures and schedules for sharing data, samples, and results of analyses with other natural resource trustees and with ARCO, the primary responsible party, and the State's decision to proceed with a type B natural resource damage assessment. The Plan also contains a list of the hazardous substances released and sources of those releases, and the results of the confirmation of exposure to natural resources in the Clark Fork River Basin. Finally, the Plan presents resource-by-resource research plans for injury determination and quantification for surface water, fisheries, sediments, and groundwater, as well as the Quality Assurance Project Plan (QAPP) for the natural resource damage assessment.

Part I of the Assessment Plan is being made available for review and comment by ARCO, other natural resource trustees, other affected Federal or State agencies or Indian Tribes,

and any other interested members of the public for a period of 30 days. Comments may be submitted in writing to:

Mr. Dick Pedersen
Natural Resource Damage Program Manager
Department of Health and Environmental Sciences
Cogswell Building
Capital Station
Helena, MT 59620.

The State may modify this Assessment Plan following its review of submitted comments. Any modifications which in the judgement of the State are significant will be made available for subsequent review and comment. At the conclusion of the assessment, the State will prepare and make available a Report of the Assessment. The report will contain a summary of the comments received on the Assessment Plan and the State's response to those comments.

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APPENDIX A: Quality Assurance Project Plan (QAPP)

LIST OF ACRONYMS

AIRS	Aerometric Information Retrieval System
ALAD	Delta-aminolevulinic Acid Dehydratase
ARCO	Atlantic Richfield Company
CECRA	Comprehensive Environmental Cleanup and Responsibility Act
CERCLA ("Superfund")	Comprehensive Environmental Response, Compensation, and Liability Act
ChE	Cholinesterase
CLP	Contract Laboratory Program
CFRSSISOP	Clark Fork River Superfund Site Investigations Standard Operating Procedures
CWA	Clean Water Act
DFWP	Montana Department of Fish, Wildlife, and Parks
DHES	Montana Department of Health and Environmental Sciences
DNRC	Montana Department of Natural Resources and Conservation
DOI	United States Department of the Interior
GIS	Geographic Information System
ICAPES	Inductively Coupled Argon Plasma Emission Spectrometry
IFIM	Instream Flow Incremental Methodology
MPTP	Montana Pole and Treatment Plant
MR	Montana Resources
NCP	National Contingency Plan
NFCRC	National Fisheries Contaminant Research Center
NPL	National Priority List
NRDA	Natural Resource Damage Assessment
NRDP	Montana Natural Resource Damage Program
PAH	Polycyclic Aromatic Hydrocarbon
PCP	Pentachlorophenol
PHABSIM	Physical Habitat Simulation
ppb	parts per billion
ppm	parts per million
PRP	Potentially Responsible Party
PVC	Polyvinyl Chloride
QAPP	Quality Assurance Project Plan
RI/FS	Remedial Investigation/Feasibility Study
SBC/CFR	Silver Bow Creek/Clark Fork River

LIST OF ACRONYMS

SDWA	Safe Drinking Water Act
SOP	Standard Operating Procedure
U.S. EPA	United States Environmental Protection Agency
USFWS	United States Fish & Wildlife Service
USGS	United States Geological Survey
VB	Valley Bottom Type
WUA	Weighted Usable Area

1.0 INTRODUCTION

1.1 CASE HISTORY AND DESCRIPTION OF ASSESSMENT PLAN CONTENT

The State of Montana ("the State") has commenced an action against the Atlantic Richfield Company ("ARCO") in the United States District Court for the District of Montana (Civil Action No. CV 83-317-HLN-CCL) pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act ("CERCLA"), 42 U.S.C. §§ 9601-9675, and the Montana Comprehensive Environmental Cleanup and Responsibility Act ("CECRA"), Mont. Code Ann. §§ 75-10-701 to 75-10-724. In this action, Montana seeks to recover damages for injuries to natural resources resulting from releases of hazardous and/or deleterious substances¹ from facilities for which ARCO is the primary responsible party. The State of Montana has begun to assess the natural resource damages in accordance with the regulations of the U.S. Department of the Interior (DOI) as set forth in 43 CFR Part 11.

Figure 1 presents the steps outlined in the DOI's regulations for conducting natural resource damage assessments of this type.² In October, 1991, the State completed the first phase of the damage assessment process when it released its Preassessment Screen (Montana NRDP 1991). The purpose of the Preassessment Screen was to determine whether a discharge or release of hazardous substances warranted conducting a full-scale assessment. In its Screen, the State of Montana determined that:

- Releases of hazardous substances have occurred;
- Natural resources for which the State of Montana can assert trusteeship have been, or are likely to be, adversely impacted by the releases;
- The quantity and concentration of the released substances are sufficient to potentially cause injury to those natural resources;
- Data sufficient to pursue an assessment are readily available or likely to be obtained at reasonable cost; and
- Response actions carried out or planned pursuant to the Superfund Remedial Investigation/Feasibility Study (RI/FS) program will not sufficiently remedy the injury to natural resources without further action.

¹ Hereafter, references to "hazardous substances" includes "hazardous and/or deleterious substances."

² This is a "type B" damage assessment. See Assessment Plan at section 4.0.

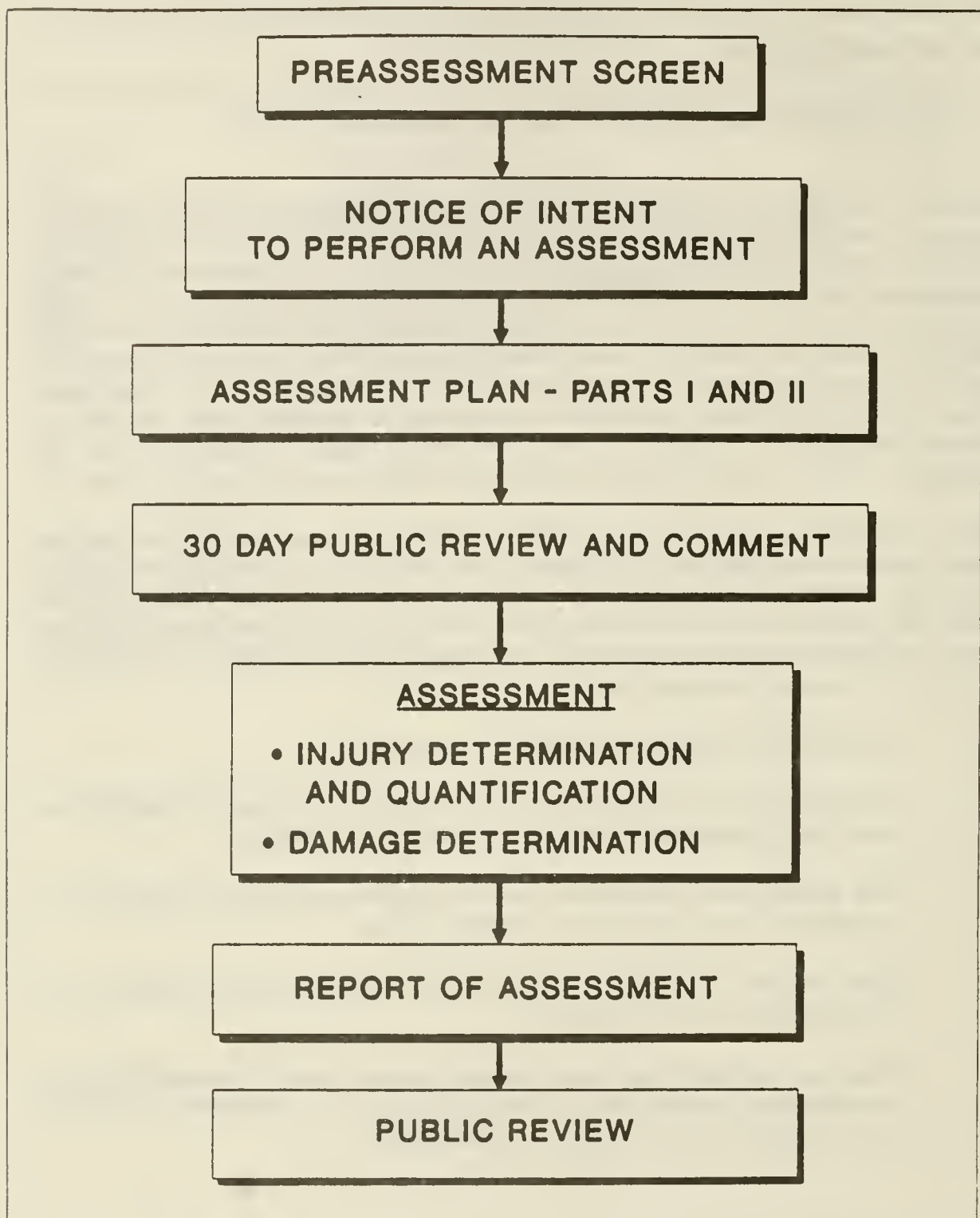


Figure 1. Clark Fork NPL Sites Natural Resource Damage Assessment: Administrative Sequence

In addition, the State determined that:

- ARCO is responsible for multiple and at times continuous releases of hazardous substances in the Clark Fork River Basin and vicinity;
- Hazardous substances released include, but are not limited to, arsenic, beryllium, cadmium, copper, creosote, lead, pentachlorophenol, polycyclic aromatic hydrocarbons, selenium, silver, volatile organic compounds, and zinc;
- The releases of hazardous substances from the four National Priority List (NPL) "Superfund" sites for which ARCO is the primary responsible party (Silver Bow Creek/Butte Area, Montana Pole, Anaconda Smelter, and Milltown Reservoir/Clark Fork River) have been in sufficient quantity, concentration, and duration to have injured the natural resources of the Clark Fork River Basin and surrounding areas; and
- Natural resources potentially injured by the releases of hazardous substances include surface water, groundwater, soils, sediments, vegetation, fish and other aquatic biota, wildlife, and air.

The Preassessment Screen contained documentation on the time, quantity, duration, and frequency of releases of hazardous substances from the four NPL sites, sources of hazardous substances released, and pathways by which natural resources potentially have been exposed to hazardous substances. In addition, the Screen identified exposed areas in the Clark Fork River Basin, presented examples of concentrations of hazardous substances in different media, and identified potentially affected resources and associated services.

On the basis of the findings of the Preassessment Screen, the State determined to proceed with an assessment and submitted a Notice of Intent to Proceed with an Assessment to ARCO. The Notice, in part, provided ARCO with the opportunity to submit to the State an Assessment Plan. Subsequent to this, ARCO submitted its written comments on the Preassessment Screen to the State. ARCO did not submit an Assessment Plan, and it did not indicate any intention to do so in the future.

This Assessment Plan represents the next phase in the assessment process. The purpose of this Assessment Plan is to ensure that the assessment is performed in a planned and systematic manner. The Assessment Plan identifies those scientific and economic method-

ologies that are expected to be performed in the assessment. The Assessment Plan includes:

"descriptions of the natural resources and the geographical areas involved...sampling locations within those geographical areas, sample and survey design, numbers and types of samples to be collected, analyses to be performed, preliminary determination of the recovery period, and other such information required to perform the selected methodologies." [43 CFR § 11.31 (a)(2)]

The Plan also includes:

- Information sufficient to demonstrate coordination with remedial investigation and feasibility studies (RI/FS) [43 CFR § 11.31(a)(3)];
 - Procedures and schedules for sharing data, split samples, and results of analyses with natural resource trustees and ARCO, the primary responsible party [43 CFR § 11.31(a)(4)];
 - Explanation of the decision to proceed with a type B assessment [43 CFR § 11.31(b)];
 - The results of confirmation of exposure of natural resources to hazardous substances [43 CFR § 11.31(c)(1)];
 - The Economic Methodology Determination performed in accordance with the guidance provided in 43 CFR § 11.31 (c)(2);
 - A Quality Assurance Plan in accordance with the National Contingency Plan (NCP) and applicable U.S. EPA guidance for quality control and quality assurance plans [43 CFR § 11.31(c)(3)]; and
 - The objectives of any testing and sampling for injury and pathway determination [43 CFR § 11.31(c)(4)].
-

Public Review and Comment

In accordance with the DOI regulations, the Assessment Plan is being made available for review and comment by ARCO, other natural resource trustees, other affected Federal or State agencies or Indian Tribes, and any other interested members of the public for a period of 30 days. Comments may be submitted in writing to:

Mr. Dick Pedersen
Natural Resource Damage Program Manager
Department of Health and Environmental Sciences
Cogswell Building
Capital Station
Helena, MT 59620.

The State may modify this Assessment Plan following its review of submitted comments. Any modifications which in the judgement of the State are significant will be made available for subsequent review and comment. At the conclusion of the assessment, the State will prepare and make available a Report of the Assessment. The report will contain a summary of the comments received on the Assessment Plan and the State's responses to those comments.

Scope of Assessment Plan: Part I

Part I of the Assessment Plan addresses activities associated with injury determination and quantification phases for four potentially injured natural resources: surface water resources, fisheries resources, sediment resources, and groundwater resources. Part II of the Assessment Plan, which will be completed and made available in the spring of 1992, will contain methodologies for conducting injury determination and quantification for soil resources, vegetation resources, wildlife resources, and air resources, a preliminary determination of recovery periods for potentially injured resources, as well as methodologies for assessing economic damages. Part II of the Assessment Plan will be made available for another 30-day public review and comment period.

This Assessment Plan was prepared by RCG/Hagler, Bailly, Inc. under contract to the State of Montana.

1.2 ORGANIZATION OF ASSESSMENT PLAN

Part I of the Assessment Plan is organized as follows: Section 2.0 describes coordination of the assessment with investigations conducted pursuant to the Remedial Investigation/Feasibility Study (RI/FS) process currently underway at the four NPL sites in the Clark Fork River Basin. Section 3.0 describes procedures and schedules for sharing

data, samples, and results of analyses with other natural resource trustees and with ARCO, the primary responsible party. Section 4.0 contains documentation of the State's decision to proceed with a type B assessment. Section 5.0 contains a list of the hazardous substances released and sources of those releases. Section 6.0 contains the results of the confirmation of exposure. Section 7.0 contains resource-by-resource research plans. Section 8.0 contains literature cited in this Assessment Plan. Appendix A contains the Quality Assurance Project Plan for the assessment.

2.0 COORDINATION WITH RI/FS

The U.S. EPA has listed four NPL sites in the Clark Fork River Basin (Figure 2). The four sites are Silver Bow Creek/Butte Area, Anaconda Smelter, Milltown Reservoir, and Montana Pole. The U.S. EPA and Montana DHES have identified approximately 77 potential environmental and/or human health problems due to past mining, milling, smelting, and wood-treating activities at the four sites (U.S. EPA and Montana DHES 1990). The U.S. EPA and Montana DHES have consolidated these problems into approximately 28 operable units. As a part of the Superfund process, many activities are conducted under the authority of the U.S. EPA and Montana DHES, including preliminary assessments and site investigations, identification and notification of potentially responsible parties, emergency, time-critical and expedited response actions, preparation of work plans followed by remedial investigations and feasibility studies (RI/FS), selection of cleanup alternatives, preparation of remedial designs and implementation of remedial actions. ARCO has had substantial participation in many of these activities. It is presently estimated that the Superfund activities will continue past the year 2000 (U.S. EPA and Montana DHES 1990).

The Natural Resource Damage Program (NRDP) has coordinated its efforts with those of the Superfund programs of the U.S. EPA and Montana DHES. This includes communicating with federal and state project managers for the various operable units. Data, information and reports prepared as part of the Superfund process have been provided to the Natural Resource Damage Program. The Preassessment Screen and Assessment Plan, Part I, have been provided by the Natural Resource Damage Program to the federal and state Superfund programs. Additionally, in the context of the RI/FS Administrative Order on Consent relating to the Streamside Tailings Operable Unit of the Silver Bow Creek/Butte Area site, Montana and ARCO agreed to certain procedures to make available for consideration and inclusion in the RI/FS certain data, including data on specified characteristics collected in connection with the natural resource damage assessment.

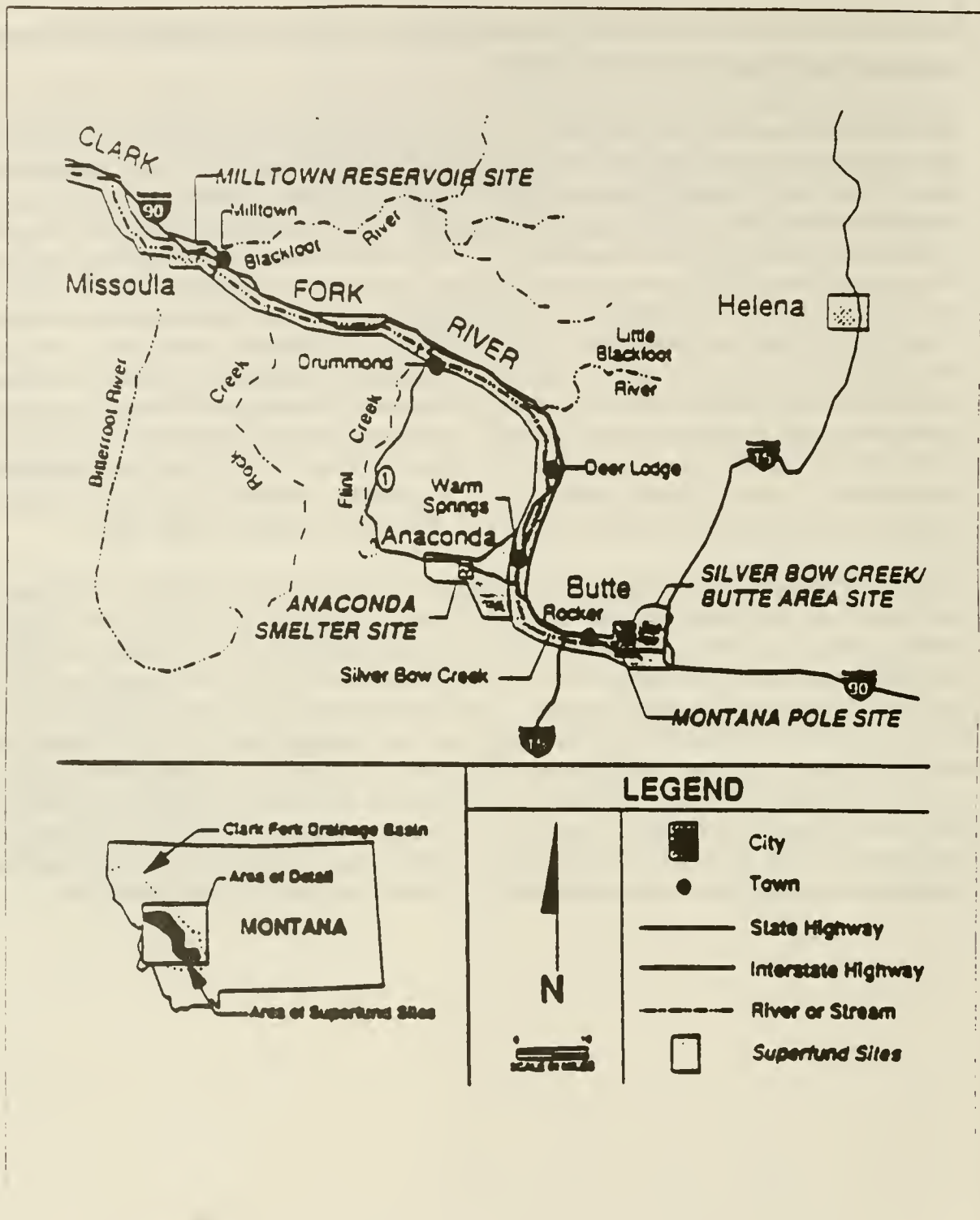


Figure 2. Location of NPL Sites in the Clark Fork River Basin (U.S. EPA and MDHES 1990).

3.0 PROCEDURES AND SCHEDULES FOR SHARING DATA WITH NATURAL RESOURCE TRUSTEES AND WITH ARCO, THE PRIMARY RESPONSIBLE PARTY

DOI's damage assessment regulations provide that the assessment plan may include:

"...procedures and schedules for sharing data, split samples, and results of analyses, when requested, with any identified potentially responsible parties and other natural resource trustees." [43 CFR § 11.31(a)(4)]

The State of Montana intends to act in accordance with this provision, as described below.

3.1 PROCEDURES AND SCHEDULES FOR SHARING DATA AND RESULTS OF ANALYSES

In order to facilitate the data-sharing process, natural resource trustees and ARCO will be provided with an opportunity to obtain valid data from individual studies. If natural resource trustees and/or ARCO wish to receive such valid data, a written request should be submitted to the State's Natural Resource Damage Program (NRDP) identifying those data which are desired. The NRDP will then provide the valid data after it is available.

3.2 PROCEDURES AND SCHEDULES FOR SPLIT SAMPLES

When samples are to be taken in the field for analysis, the NRDP will provide notice of the timing and location of field sample collection in order to provide natural resource trustees and ARCO with an opportunity to collect appropriate duplicate samples. Parties wishing to receive such notification should submit a written request in advance to the NRDP.

4.0 DECISION TO PERFORM TYPE B ASSESSMENT

43 CFR § 11.33 states that the State of Montana may select between performing a type A or a type B natural resource damage assessment. The State of Montana intends to perform a type B assessment. Currently type A assessments -- intended to be applied to "simplified assessments requiring minimal field observation" [CERCLA § 301 (c)(2)(A)] -- have only been developed by DOI for releases to coastal and marine environments. In this case, the Clark Fork River Basin is not a coastal or a marine environment, the discharges and releases of hazardous substances have occurred for a long duration (over 100 years), the discharges and releases cannot be considered minor, and the discharges and releases have been multiple and at times continuous over a large geographic area. Type A assessment methodologies thus would be inappropriate for this assessment.

5.0 HAZARDOUS SUBSTANCES RELEASED

The Preassessment Screen (Montana NRDP 1991, Section 2.4) provided a preliminary list of hazardous substances that have been released from Clark Fork NPL sites for which ARCO is the primary responsible party. These hazardous substances include, but may not be limited to, arsenic, beryllium, cadmium, copper, creosote, lead, pentachlorophenol, polycyclic aromatic hydrocarbons, selenium, silver, volatile organic compounds, zinc, as well as related compounds of the above.

5.1 SOURCES OF HAZARDOUS SUBSTANCES

Numerous sources associated with the four NPL sites have been identified as having resulted in releases and re-releases of the hazardous substances identified above. For example, the Silver Bow Creek/Butte Area contains about 150 major rock dumps, covering 350 acres (142 ha) and containing an estimated 9.85 million yd³ (7.54 million m³) of waste (U.S. EPA and Montana DHES 1990). CH₂M Hill and Chen-Northern (1990) identified three primary sources of hazardous substances in the Area I Operable Unit of Silver Bow Creek: (1) the Parrot Smelter tailings and waste deposits, located 10-30 ft (3-9 m) below the surface, amounting to about 650,000 yd³ (497,000 m³) of waste material; (2) the Butte Reduction Works tailing impoundments and slag deposits, amounting to 1.6 million yd³ (1.2 million m³) of waste; and (3) the Colorado Tailings, amounting to 600,000 yd³ (459,000 m³) of waste. Other sources of hazardous substances in the Butte area include the 750 acre (304 ha) Yankee Doodle Tailings ponds and the 1,400 acres (567 ha) of leach pads and waste dumps north and northeast of the Berkeley Pit (Camp Dresser & McKee 1990a).

The U.S. EPA and Montana DHES (1990) estimated that the Anaconda area contains 185 million yd³ (142 million m³) of tailings, 27 million yd³ (21 million m³) of furnace slags, and 300,000 yd³ (230,000 m³) of flue dust. The Old Works Operable Unit contains 1.46 million yd³ (1.12 million m³) of "red sands", a mixed slag and jig composition, as well as 500,000 yd³ (383,000 m³) of black slag, 274,000 yd³ (210,000 m³) of heap roast slag, and 291,000 yd³ (223,000 m³) of tailings (Tetra Tech 1987). The Opportunity Ponds contain 435 million yd³ (333 million m³) of tailings, and the Anaconda Ponds contain 290 million yd³ (222 million m³) of tailings (Tetra Tech 1987).

Smelters located in Butte and Anaconda represent sources of airborne hazardous substances released into the Basin. For example, stack arsenic emissions from the Anaconda smelter were 75 tons (68 tonnes) per day in 1917 (Taskey 1972). Tetra Tech (1987) concluded that the stack released significant quantities of arsenic, based on soils downwind of the stack that contain at least 100 ppm arsenic (ten times the suggested background concentration). Tetra Tech (1987) found that the mass of arsenic in nearby soils is close to 20 million kg (22,000 tons) within a 68,000 acre (27,500 ha) affected area.

The Montana Pole site contains numerous sources of hazardous substances. Camp Dresser & McKee (1989) found that spillage of treatment products, leaking underground storage tanks and pipes, and uncontained drainage of hazardous substances has contaminated 8.4 million ft³ (238,000 m³) of groundwater and 2.0 million ft³ (56,600 m³) of soil near the treatment plant. This contamination is seeping into Silver Bow Creek at an estimated two to five gallons (7.6-19 L) per day (U.S. EPA and Montana DHES 1990).

Camp Dresser & McKee (1990b) identified sources of hazardous substances that have accumulated at the Milltown Reservoir NPL Site. These sources include the drainage of the Butte area by Silver Bow Creek and the Clark Fork River prior to the construction of Warm Springs Pond #1 in 1911, plus numerous periods of overflow from, or bypasses around, the ponds, and periods of inadequate operation of the ponds by the Anaconda Company. The discharge from the Warm Springs Ponds contains hazardous substances (Ingman and Kerr 1990). Thus, the ponds represent a significant source. Camp Dresser & McKee (1990b) also cite Warm Springs Creek as a source of hazardous substances, as Warm Springs Creek drains the Anaconda Smelter area and flows into the Clark Fork River with no treatment. The estimated 6.0 million yd³ (4.6 million m³) of sediments behind the Milltown Dam are a source of hazardous substances for natural resources in the area (U.S. EPA and Montana DHES 1990).

6.0 CONFIRMATION OF EXPOSURE

A natural resource has been "exposed" to a hazardous substance if "all or part of a natural resource is, or has been, in physical contact with...a hazardous substance, or with media containing the...hazardous substance" [43 CFR § 11.14(q)]. According to 43 CFR § 11.34, the Assessment Plan should confirm that

"at least one of the natural resources identified as potentially injured in the preassessment screen has in fact been exposed to the...hazardous substance." [43 CFR § 11.34(a)(1), emphasis added]

The regulations state that "whenever possible, exposure shall be confirmed using existing data" from previous studies of the assessment area [43 CFR § 11.34(b)(1)]. The following sections provide confirmation of exposure for many of the potentially injured resources within the Clark Fork River Basin.

It should be recognized that the following discussion provides limited examples, using existing data, sufficient to confirm exposure of natural resources to hazardous substances (as defined above). This section is neither intended to be a comprehensive quantification of all exposed areas in the basin, nor is it intended to determine or quantify all of the injuries to natural resources.

6.1 SURFACE WATER RESOURCES

Extensive documentation exists confirming exposure of surface water resources of the Clark Fork Basin to hazardous substances. Concentrations of copper, cadmium, zinc, and lead often exceed U.S. EPA water quality criteria for aquatic life³ (see Table 1) in Silver Bow Creek, Warm Springs Ponds, and in the main stem of the Clark Fork River as far as Missoula (Ingman and Kerr 1990). These elevated metals concentrations are the result of the years of mining activities in the region rather than the result of natural processes within this mineralized area. Surface water of other streams within the mineral-rich Boulder Batholith that underlies Butte has been analyzed for heavy metal content, and cadmium, copper, lead, and zinc concentrations typically are well below the U.S. EPA water quality criteria (CH₂M Hill and Chen-Northern 1989). By contrast, 75% of monthly average cadmium concentrations from four Silver Bow Creek sampling stations exceeded the chronic

³ Although the U.S. EPA water quality criteria for the protection of freshwater aquatic life were developed with "acid-soluble" metals as criteria, U.S. EPA "recommends applying the criteria using the total recoverable method" of measuring heavy metals concentrations in surface water (50 FR 30787, 30789, 30791, 52 FR 6214). Metals concentrations described in this document refer to total recoverable metals unless otherwise noted.

Table 1. Water quality criteria for the protection of freshwater aquatic life established under Section 304(a)(1) of the Clean Water Act.

Metal	Hardness (ppm as CaCO ₃)	Acute Tox. ¹ (ppb)	Chronic Tox. ² (ppb)	Source
Cadmium	100	3.9	1.1	50 FR 30787
	200	8.6	2.0	
Copper	100	18	12	50 FR 30789
	200	34	21	
Lead	100	83	3.2	50 FR 30791
	200	200	7.7	
Zinc	100	120	110	52 FR 6214
	200	210	190	

¹ Acute toxicity criterion is defined as a one-hour average concentration that should not be exceeded more than once in a three-year period.

² Chronic toxicity criterion is a four-day average concentration that should not be exceeded more than once in a three-year period.

criterion for cadmium in FY 1989, while 100% of monthly average copper and zinc concentrations exceeded acute toxicity criteria in FY 1988 and 1989 (Ingman and Kerr 1990). Below Rock Creek, 9% of monthly average copper concentrations exceeded the acute water quality criterion (Ingman and Kerr 1990). The Phase I RI/FS data from Silver Bow Creek found that Silver Bow Creek copper concentrations exceeded chronic water quality criteria in 100% of the samples (U.S. EPA 1990). During FY 1985-1987, the average annual concentrations of copper and zinc in Silver Bow Creek were ten to over 20 times the chronic toxicity criterion (Johnson and Schmidt 1988).

Downstream of Warm Springs Ponds on the Clark Fork River, metals concentrations in FY 1988-1989 exceeded chronic toxicity criteria for cadmium, copper, and lead (Ingman and Kerr 1990). Water quality data from FY 1985 show concentrations of copper and zinc as high as 60 ppb and 279 ppb, respectively, at the mouth of the Mill-Willow Bypass, and 40 ppb and 136 ppb, respectively, below the Warm Springs Creek confluence with the Clark Fork River (Montana DHES 1986). Further downstream in the Clark Fork, Phillips (1985) found copper and zinc concentrations as high as 300 ppb copper and 350 ppb zinc at Deer Lodge. During spring runoff, copper concentrations near Drummond have been measured at levels nearly ten times the acute criterion (Montana DNRC 1988).

Such contaminated conditions have existed in Silver Bow Creek and the Clark Fork River for many years. For example, a water quality study prepared by the U.S. EPA (1972) found average copper concentrations in the Clark Fork to be three to six times higher than today's acute toxicity criterion as far downstream as Garrison, MT.

6.2 BIOLOGIC RESOURCES: FISHERIES

Fish in the Clark Fork River have been and continue to be exposed to hazardous substances through both direct exposure to contaminated surface water and sediments (see Section 6.3), as well as through food-chain exposures to contaminated prey. Thus, Section 6.1, confirmation of exposure to surface water, serves as confirmation of exposure to all organisms which live in surface water. "Exposure," as defined at 43 CFR § 11.14 (q), occurs when "all or part of a natural resource is, or has been, in physical contact with...a hazardous substance, or with media containing...a hazardous substance." If surface waters of the Clark Fork River and Silver Bow Creek contain hazardous substances, as shown in section 6.1, aquatic biota will have been exposed as well.

Existing data demonstrating elevated concentrations of hazardous substances in fish tissues also confirm exposure to fisheries. Brown trout (*Salmo trutta*) collected in the Clark Fork River have been shown to have elevated concentrations of hazardous substances in liver and kidney samples. For example, Phillips and Spoon (1990) reported copper concentrations as high as 1,663 ppm in liver tissues and approximately 5.5 ppm of cadmium in kidney tissue. In addition, the Montana Department of Fish, Wildlife, and Parks (DFWP) conducted

analyses of copper and cadmium in gill tissue of brown trout collected from the Clark Fork River following three documented fish kills in 1984, 1988, and 1989 (Phillips 1984, 1988, 1989). Results showed elevated levels of both copper and cadmium in gill tissues of brown trout, longnose suckers (*Catostomus catostomus*), and mountain whitefish (*Prosopium williamsoni*). For example, data from 1984 (Phillips 1984) showed average copper and cadmium concentrations in gill tissue (washed samples, expressed on dry weight basis) of 26.5 ppm and 1.1 ppm, respectively. Concentrations in gill tissue samples of brown trout, longnose suckers, and mountain whitefish analyzed following a 1988 fish kill (Phillips 1988) ranged from 22-228 ppm of copper, and 116-233 ppm of zinc. Data from a fish kill in 1989 (Phillips 1989) showed concentrations in brown trout ranging from 4.0-6.4 ppm of cadmium in gill tissues, 407-812 ppm copper in gill tissues and 409-1,641 ppm copper in liver tissues, and 628-1,309 ppm zinc in gill tissues (all values on dry weight basis).

6.3 GEOLOGIC RESOURCES: SOILS/SEDIMENTS

Numerous studies have confirmed that soils and sediments in the upper Clark Fork Basin have been exposed to hazardous substances (see Table 2 for selected examples). To place the data shown in Table 2 in perspective, CH₂M Hill *et al.* (1991) suggest that appropriate "background" soil concentrations are 16 ppm for arsenic, 29 ppm for copper, 15 ppm for lead, and 82 ppm for zinc. Arsenic has been measured in soils near Anaconda (see Taskey 1972 reference, Table 2) at concentrations nearly 150 times higher than these background levels. Similarly, copper concentrations have been found almost 300 times higher than the suggested background concentration, zinc concentrations almost 40 times background levels, and lead concentrations 100 times higher than background concentrations (Taskey 1972). CH₂M Hill *et al.* (1991) report soil concentrations along the Clark Fork River as high as 1,100 ppm arsenic (68 times background, with 95% of all samples exceeding suggested phytotoxic levels of 100 ppm), 87,100 ppm copper (3,000 times background, with 95% of all samples exceeding phytotoxic concentrations of 100 ppm), and 13,300 ppm zinc (162 times background, with 100% of all samples exceeding phytotoxic levels of 500 ppm).

Metals concentrations are also significantly elevated in the floodplain and in irrigated soils in the basin, as well as in soils downwind of the smelters in Butte and Anaconda. Near Anaconda, Taskey (1972) found soils contaminated with 2,362 ppm arsenic, 8,450 ppm copper, 1,500 ppm lead, and 3,100 ppm zinc. Rice and Ray (1985) found soil arsenic levels of 1,103 ppm at a depth of four to twelve centimeters (1.8 - 5.5 inches) below ground near Grant-Kohrs Ranch (Deer Lodge, MT). Soil concentrations in the Anaconda area measured by Tetra Tech (1987) have been as high as 1,660 ppm arsenic, 62 ppm cadmium, 2,330 ppm copper, 1,000 ppm lead, and 1,190 ppm zinc.

Table 2. Exposure of geologic resources to hazardous substances: concentrations in soils and sediments at Clark Fork NPL Sites.

Concentration (ppm)							
NPL Site	Area/Operable Unit (Medium)	As	Cd	Cu	Pb	Zn	Reference
Silver Bow Creek/ Butte Area	Colorado Tailings: Peat (soil)	1,550 (max) 821 (\bar{x})		14,300 (max) 6,022 (\bar{x})	14,900 (max) 9,933 (\bar{x})	23,500 (max) 17,333 (\bar{x})	Thornell 1985 (in Johnson and Schmidt 1988)
	Colorado Tailings (sediments)			3,900	530	12,000	Peckham 1979
	Ramsay (sediments)			5,400	1,900	5,500	
	Miles Crossing (sediment)			20,000	13,000	22,000	
Silver Bow Creek/ Butte Area	Warm Springs Pond #2 (sediments)	294	103	3,940	542	12,100	MultiTech 1987
	Warm Springs Pond #3 (sediments)	422	193	5,170	183	32,300	
Anaconda Smelter	- Opportunity (soil)	370	5.2	583	111	197	Tetra Tech 1987
	- Valley (soil)	430	10.2	1,679	146	608	
	- Inversion (soil)	157	6.6	350	95	295	
	- Crackerville (soil)	1,660	62	2,330	1,000	1,190	
Anaconda Smelter	- maximum soil concentrations near Anaconda (soil)	2,362		8,450	1,500	3,100	Taskey 1972
Milltown Reservoir	Clark Fork River (floodplain sediments)						Ray 1983 (in Johnson and Schmidt 1988)
	- Racetrack	402	11.6	2,375			
	- Garrison	629	5.0	1,587			
	- Drummond	578	12.9	4,155			

Table 2 (con't).

Concentration (in ppm, unless otherwise noted) Note: $\mu\text{g/kg} = \text{ppb}$			
NPL Site	Area/Operable Unit (Medium)	PCP	Reference
Montana Pole	On-Site Soil (Soil)	4,000 (max)	Camp Dresser and McKee 1989
	Facility Yards (Soil)	3,500 (max)	
Montana Pole	Outside Fenced Area (Soil)	1,026 $\mu\text{g/kg}(\bar{x})$	Camp Dresser and McKee 1990c
	Inside Fenced Area (Soil)	42,863 $\mu\text{g/kg}(\bar{x})$	

The soil around the Montana Pole site has been shown to be contaminated to such a degree that the U.S. EPA removed 12,000 cubic yards (9,180 m³) of the soil in 1987. Pentachlorophenol (PCP) was found in soil at levels as high as 4,000 ppm within the Montana Pole facility (Camp Dresser and McKee 1989).

Axtmann and Luoma (1991) reported average concentrations of metals in bed sediments of Clark Fork tributaries "least influenced by mining" to be <0.3 ppm for cadmium, 14-27 ppm for copper, 9-13 ppm for lead, and 45-60 ppm for zinc. As shown in Table 2, Peckham (1979) found metals concentrations in Silver Bow Creek as high as 20,000 ppm copper, 13,000 ppm lead, and 22,000 ppm zinc -- concentrations as much as 1,000 times greater than these suggested background concentrations. In Warm Springs Pond #3, sediments have been found to contain 422 ppm arsenic, 193 ppm cadmium (>40 times background), 5,170 ppm copper (190-370 times background) and 32,300 ppm zinc (540-700 times background) (MultiTech 1987). River sediments in the Clark Fork from Warm Springs Ponds to Milltown Reservoir contain concentrations of arsenic, cadmium, copper, lead, and zinc orders-of-magnitude greater than these suggested background levels. For example, Ray (1983, in Johnson and Schmidt 1988) measured concentrations as high as 629 ppm of arsenic, 12.9 ppm of cadmium, and 4,155 ppm of copper (150-450 times background) in fluvial sediments in the floodplain of the Clark Fork River near Drummond. In Milltown Reservoir, some 120 river miles (193 km) downstream, sediments have been found to contain 320 ppm arsenic, 14.9 ppm cadmium, 2,182 ppm copper (80-150 times background), and 4,045 ppm zinc (67-90 times background) (Moore 1985).

In the Anaconda area, PTI (1990) measured concentrations in channel sediments (in the Smelter Hill drainage) of 3,300 ppm arsenic, 46.7 ppm cadmium, 8,650 ppm copper (320-615 times background), 2,480 ppm lead (190-275 times background), and 4,220 ppm zinc (70-90 times background).

6.4 GROUNDWATER RESOURCES

Groundwater resources have been exposed to hazardous substances in a number of areas including Silver Bow Creek/Butte Area, Montana Pole, Anaconda Smelter, and Milltown Reservoir. Selected examples of existing data are provided in Table 3.

Water samples taken in the Berkeley Pit -- which is filling with groundwater from the Butte aquifer -- have shown extremely elevated concentrations of arsenic (1,380 ppb), cadmium (1,860 ppb), copper (213,000 ppb), lead (576 ppb), and zinc (505,000 ppb) (Camp Dresser & McKee 1988, in Johnson and Schmidt 1988). Further evidence of widespread contamination in the Butte Hill area is illustrated by groundwater obtained from the Travona Mine in January and February 1989: groundwater had mean concentrations of 177 ppb arsenic (Duaime *et al.* 1989).

Table 3. Exposure of groundwater to hazardous substances: examples at Clark Fork River NPL Sites

Concentration (in ppb = $\mu\text{g/l}$)								
NPL Site	Area/Operable Unit	As	Cd	Cu	Pb	Zn	Reference	
Silver Bow Creek/ Butte Area	Berkeley Pit						Camp Dresser and McKee 1988 (in Johnson and Schmidt 1988)	
	-Depth 216 ft (65.8m)	1,290	1,850	213,000	343	500,000		
	-Depth 426 ft (129.8m)	1,380	1,860	209,000	576	505,000		
Silver Bow Creek/ Butte Area	Colorado Tailings	140	520	54,100		159,000	Dusime <i>et al.</i> 1985	
Silver Bow Creek/ Butte Area	Area One (maximum concentrations)	158	1,780	49,200	3,520	31,600	CH ₂ M Hill and Chen-Northern 1990	
Silver Bow Creek/ Butte Area	Near Warm Springs Ponds	244 (dissolved)		38 (dissolved)	25 (dissolved)	400 (dissolved)	MultiTech 1987	
Anaconda Smelter	Smelter Hill	3,820	3.6		49	7,100	PTI 1990	
Anaconda Smelter	- saturated tailings (maximum concentrations)	3,600	68	51		1,038	Tetra Tech 1987	
Anaconda Smelter	Opportunity Ponds	24		37		166	Tetra Tech 1986 (in Johnson and Schmidt 1988)	
Milltown Reservoir	Wells along Clark Fork River	170	14 11				CH ₂ M Hill <i>et al.</i> 1991	
Montana Pole	Wells at Milltown Dam	102	7	180	80	1,570	Montana Power Co. 1987 (in Johnson and Schmidt 1988)	
				50,000		100,000	Camp Dresser and McKee 1990c	

Concentration (ppb)								
NPL Site	Area/Operable Unit	PCP	Acenaphthene	Total Xylenes	Toluene	Benzene	Ethyl-Benzene	Reference
Montana Pole	- Process Area - near Silver Bow Creek	47,100 71,900						Keystone 1991
Montana Pole		1,100,000 880,000	2,480,000	540	57	17	16	Camp Dresser and McKee 1990c

CH₂M Hill and Chen-Northern (1990) documented dissolved concentrations of copper in excess of 490,000 ppb, zinc in excess of 300,000 ppb, lead in excess of 3,500 ppb, arsenic in excess of 800 ppb, and cadmium in excess of 1,700 ppb in the upper alluvial aquifer near Silver Bow Creek in Butte.

Groundwater samples taken near the Montana Pole NPL Site between December 1984 and July 1985 contained 10,000-160,000 ppb pentachlorophenol (PCP), while groundwater samples taken in August 1985 contained PCP concentrations from 25 ppb to 1,100,000 ppb. PCP concentrations up to 880,000 ppb, and acenaphthene concentrations up to 2,480,000 ppb were detected in groundwater during the period 1988-1990 (Camp Dresser & McKee 1990c). Xylenes (7.9-540 ppb), toluene (5.5-57 ppb), benzene (1.2-17 ppb), and ethylbenzene (1.7-16 ppb) were also detected at that time (Camp Dresser & McKee 1990c).

PTI (1990) analyzed samples of groundwater from the Smelter Hill Operable Unit near Anaconda. Concentration maxima included 3,820 ppb of arsenic and 7,100 ppb of zinc. Tetra Tech (1987) obtained concentrations in groundwater near Anaconda as high as 9,110 ppb arsenic, 502 ppb cadmium, and 58,400 ppb zinc. Tetra Tech (1987) documented 21 exceedences of primary drinking water standards for arsenic, and 12 exceedences of drinking water standards for cadmium.

Groundwater at the Milltown Reservoir NPL site was found to contain concentrations of arsenic exceeding 10,000 ppb, zinc over 300 ppb, and copper exceeding 180 ppb (ENSR 1989; Woessner *et al.* 1984; Montana Power 1987, in Johnson & Schmidt 1988). Wastes trapped in the sediments have contaminated the groundwater in the reservoir sediments, and this water has migrated northward contaminating four wells serving 34 households and degrading the quality of a well serving a restaurant (Woessner *et al.* 1984). Groundwater north and west of the reservoir exceeded primary drinking water standards for arsenic.

6.5 BIOLOGIC RESOURCES: VEGETATION

Residues of hazardous substances have been measured in vegetation in the Deer Lodge Valley in areas with elevated concentrations of hazardous substances in soil.⁴ Munshower (1977) compared cadmium levels in plants 15 miles northeast of Anaconda with plants in a control site near Bozeman. Cadmium concentrations in barley were eight times higher in Deer Lodge Valley plants than in plants from the control site.

⁴ As in the case of fisheries exposure being confirmed through the confirmation of exposure for surface water, confirmation of exposure to soils serves as a confirmation of exposure to vegetation (in areas which are vegetated).

PTI (1990) analyzed 387 vegetation samples from Smelter Hill for acid extractable metals. Plants sampled at horsebrush sites were found to contain the highest concentrations of the hazardous substances arsenic, cadmium, copper, lead, and zinc. Values ranged from (mean in parenthesis) 14-239 (100) ppm arsenic; 0.7-14 (5.1) ppm cadmium; 46-1,500 (467) ppm copper; 8.7-239 (82) ppm lead; and 57.6-1,570 (432) ppm for zinc. Suggested ranges of background metals concentrations in plant tissue are 0.02-7.0 ppm for arsenic, 0.1-2.4 ppm for cadmium, 5.0-20 ppm for copper, 0.2-20 ppm for lead, and 1.0-400 ppm for zinc (Alloway 1990). Of the 387 tissue analyses performed (PTI 1990), 100% of the samples exceeded the highest suggested background concentration for arsenic and copper, while the mean cadmium, lead, and zinc concentrations exceeded the highest suggested background concentrations. PTI (1991) found correlations between concentrations of arsenic, cadmium, copper, lead, and zinc in the upper two inches (5 cm) of surface soil, and concentrations of these hazardous substances in plant tissues. PTI (1991) stated that this reflects the "recent common origin" of metals contamination (i.e., anthropogenic source, rather than of geologic origin) at the Smelter Hill Site.

6.6 AIR

Emissions from stacks at the Anaconda Smelter Complex, and from smelters and roasters that operated in Butte prior to the construction of the smelters in Anaconda, released hazardous substances (including arsenic, cadmium, copper, lead, and zinc) into the air (Wake 1972), and re-entrainment of material from waste storage areas and unconfined tailings containing high concentrations of hazardous substances may continue to release hazardous substances into the air (TetraTech 1987).

Stack emissions to the atmosphere from the Anaconda Smelter Complex contained oxides of the hazardous substances arsenic, copper, cadmium, lead, and zinc (TetraTech 1987). Harkins and Swain (1907) analyzed stack emissions and found that the daily release from the main chimney averaged 59,270 lbs (26,849 kg) arsenic trioxide, 4,340 lbs (1,966 kg) copper, 4,775 lbs (2,163 kg) lead, and 17,840 lbs (8,082 kg) iron and aluminum oxides. Between 1911 and 1916, the Anaconda Smelter Smoke Commission reported yearly averages of arsenic discharges ranging from 40 to 62 tons per day (Wells 1920, in Taskey 1972). During World War I, arsenic emissions were estimated at 75 tons per day (Wells 1920, in Taskey 1972). In 1962, the arsenic content of Anaconda's air averaged $0.45 \mu\text{g}/\text{m}^3$ and was among the highest concentrations in the country (Montana Board of Health 1962, in Wake 1972).

TetraTech (1987) summarized air quality data collected near Mill Creek and the Anaconda Smelter NPL site between 1984 and 1986 by the Anaconda Minerals Company and the Air Quality Bureau of the Montana DHES. Measured values of hazardous substances were as high as $0.221 \mu\text{g}/\text{m}^3$ (average of 0.016) for arsenic, $0.092 \mu\text{g}/\text{m}^3$ for cadmium (average of 0.009), and $1.22 \mu\text{g}/\text{m}^3$ (average of 0.08) for lead. In comparison to background air quality

data collected between 1975 and 1985 (AIRS 1991) from sites located in Powell and Glacier Counties, MT, maximum concentrations of airborne arsenic near Anaconda exceeded average annual background concentrations by a factor of 80, maximum concentrations of cadmium exceeded average annual background by a factor of 150, and the maximum concentration of airborne lead exceeded the average annual background by a factor of over 100. Annual averages at the Anaconda site exceeded average annual background concentrations for arsenic, cadmium, and lead by factors of five, 15, and eight, respectively.

7.0 RESEARCH PLANS

This section describes research that has been and will be conducted during the injury determination and quantification phases of the State of Montana's assessment.

Although not specifically discussed further in the individual research plans, significant amounts of data relevant to the State's assessment have been collected by various Federal and State Agencies and their contractors, as well as by academic institutions. Much of this data has been collected as part of the RI/FS process at the four NPL sites. The State intends to use this existing data. Existing data will be evaluated by the State on the basis of quality, reliability, accuracy, timing of sample collection, spatial coverage, and other criteria, as appropriate.

The geographic focus of the State's injury assessment for surface water, fisheries, and sediments will be limited to Silver Bow Creek from Butte to Warm Springs Ponds, the Warm Springs Ponds complex, and the Clark Fork River from Warm Springs Ponds to Missoula. Groundwater studies will address the Butte/Silver Bow Creek area, the Montana Pole area, the Anaconda/Opportunity Ponds/Warm Springs Ponds area, and the Milltown Reservoir area.

All research protocols have been designed to meet quality assurance/quality control (QA/QC) project goals -- including the use of standards, instrument calibration, blanks, spikes, duplication, and chain-of-custody -- as described in the Quality Assurance Project Plan (QAPP) contained in Appendix A of the Assessment Plan: Part I.

7.1 SOURCE IDENTIFICATION

As described in Section 5.1, sources of hazardous substances released into the Clark Fork River Basin include, but are not limited to, numerous tailings deposits, tailings ponds, waste piles, flue dust piles, and smelters located throughout the Basin. Sources of hazardous substances to which natural resources have been exposed will be identified as a part of the assessment. This may include:

- Identifying sources of hazardous substances and the nature of releases and re-releases.
 - Identifying sources of hazardous substances entering Silver Bow Creek, Warm Springs Ponds, and the Clark Fork River based on surface water, groundwater, and sediment data.
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- Identifying sources of hazardous substances entering groundwater systems, based on existing data on groundwater quality, regional flow systems analysis, aquifer geometry, and other hydrologic and hydrogeologic properties, as appropriate.
 - Confirming releases of hazardous substances from smelter emissions and tailings.

7.2 PATHWAY DETERMINATION

The purpose of pathway determination is to identify pathways by which natural resources have been exposed to hazardous substances [43 CFR § 11.63 (a)(1)]. Pathways may be determined by demonstrating the presence of hazardous substances in pathway resources or by using models to demonstrate that the exposure route served as a pathway [43 CFR § 11.63 (2)].

Relevant pathways to potentially injured resources of the Clark Fork River Basin include:

- Direct contact with hazardous substances;
- Surface water pathways;
- Groundwater pathways;
- Air pathways;
- Geologic pathways, including both soils and bed, bank, and floodplain sediments; and
- Biological pathways, including vegetation, terrestrial and aquatic invertebrates, birds, mammals, and fish.

Pathway determination will include:

- Demonstration that hazardous substances are present in "sufficient concentrations" in pathway resources, including surface water, groundwater, soils, sediment, sediment pore-water, air, and terrestrial and aquatic biota [43 CFR § 11.63 (a)(2)];
 - Determination that surface water resources downstream of the sources of releases of hazardous substances have been exposed to those hazardous substances [43 CFR § 11.63 (b)(2)(i)] and that open water bodies such as the Warm Springs Ponds have been exposed to hazardous substances [43 CFR § 11.63 (b)(2)(ii)];
 - Determination that groundwater beneath or downgradient of the sources of releases of hazardous substances has been exposed to the hazardous substances [43 CFR § 11.63 (c)(2)];
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- Determination that air resources have been exposed to the releases of hazardous substances [43 CFR § 11.63 (d)(2)];
 - Determination that soils and sediments (including bed, bank, and floodplain) have been exposed to hazardous substances [43 CFR § 11.63 (e)(2)(i)]; and
 - Identification of direct exposure from physical contact and/or indirect exposure from food chain processes involving biological pathways [43 CFR § 11.63 (f)(2)].
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7.3 SURFACE WATER RESOURCES

7.3.1 Definition of Injury

Relevant definitions of injury to surface water resources of the Clark Fork River Basin include:

- Concentrations and duration of substances in excess of drinking water standards as established by sections 1411-1416 of the Safe Drinking Water Act (SDWA), or by other Federal or State laws or regulations that establish such standards for drinking water, in surface water that was potable before the discharge or release [43 CFR § 11.62 (b)(1)(i)];
- Concentrations and duration of substances in excess of water quality criteria established by section 1401(1)(D) of SDWA, or by other Federal or State laws or regulations that establish such criteria for public water supplies, in surface water that before the...release met the criteria and is a committed use [43 CFR § 11.62 (b)(1)(ii)];
- Concentrations and duration of substances in excess of applicable water quality criteria established by section 304(a)(1) of the Clean Water Act (CWA), or by other Federal or State laws or regulations that establish such criteria, in surface water that before the discharge or release met the criteria and is a committed use as habitat for aquatic life, water supply, or recreation. The most stringent criterion applies when surface water is used for more than one of these purposes [43 CFR § 11.62 (b)(1)(iii)];
- Concentrations of substances on bed, bank, or shoreline sediments sufficient to cause the sediment to exhibit characteristics identified under or listed pursuant to section 3001 of the Solid Waste Disposal Act, 42 U.S.C. 6921 [43 CFR § 11.62 (b)(1)(iv)]; and
- Concentrations and duration of substances sufficient to have caused injury to other resources when exposed to surface water, suspended or unsuspended sediments, or bed, bank, or shoreline sediments [43 CFR § 11.62 (b)(1)(v)].

7.3.2 Description of Surface Water Resources to be Assessed

As indicated in section 6.1, surface water resources that have been exposed to hazardous substances include Silver Bow Creek from Butte to Warm Springs Ponds, the Warm Springs

Ponds, and the Clark Fork River from Warm Springs Ponds to Missoula. Determination and quantification of injury to surface water resources will focus on these areas.

7.3.3 Objectives of Research Plan

Specific objectives of the surface water research plan include:

- Characterize baseline surface water conditions using control sites;
- Determine injury to surface water resources based on injury definitions presented in Section 7.3.1 by comparing water quality in exposed areas to water quality at control sites;
- Quantify injury to surface waters, including the geographic extent of injured surface waters, and the time period during which injury has occurred; and
- Review the past, present, and potential future uses of surface water in the study area.

7.3.4 Research Plan

Existing data generated by the RI/FS process, long-term ambient monitoring conducted by the Montana DHES, and other related studies will be used to assess injury to surface water resources.

Injury Determination

The injury determination phase may include the following discrete steps:

- Identify controls for quantifying baseline concentrations of hazardous substances. Selection criteria for control sites may include, as appropriate, location within similarly mineralized areas, land use characteristics, flow regime, and climatic factors;
 - Quantify baseline concentrations of hazardous substances at control sites;
 - Characterize water quality in exposed areas; and
 - Determine injury to exposed surface water resources based on evaluations of water quality criteria, drinking water standards, concentrations of hazardous
-

substances in sediments, and concentrations of hazardous substances identified in fish toxicology work as being injurious to biologic resources.

Injury Quantification

Injury quantification will entail characterizing differences from baseline in exposed areas and estimating the areal extent of injured surface water and sediments [43 CFR § 11.71 (h)(1)].

7.4 BIOLOGIC RESOURCES: FISHERIES

7.4.1 Definition of Injury

Relevant definitions of injury to biological resources includes:

"...the biological resource or its offspring...(has)...undergone at least one of the following adverse changes in viability: death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction), or physical deformations." [43 CFR § 11.62(f)(1)(i)]

The DOI has developed four "acceptance criteria" for determining injury [43 CFR § 11.62(f)(2)]:

"(i) The biological response is often the result of exposure to...hazardous substances. This criterion excludes biological responses that are caused predominately by other environmental factors such as disturbance, nutrition, trauma, or weather. The biological response must be a commonly documented response resulting from exposure to...hazardous substances.

(ii) Exposure to...hazardous substances is known to cause this biological response in free-ranging organisms. This criterion identifies biological responses that have been documented to occur in a natural ecosystem as a results of exposure to...hazardous substances. The documentation must include the correlation of the degree of the biological response to the observed exposure concentration of...hazardous substances.

(iii) Exposure to...hazardous substances is known to cause this biological response in controlled experiments. This criterion provides a quantitative confirmation of a biological response occurring under environmentally realistic exposure levels that may be linked to...hazardous substance exposure that has been observed in a natural ecosystem. Biological responses that have been documented only in controlled experimental conditions are insufficient to establish correlation with exposure occurring in a natural ecosystem.

(iv) The biological response measurement is practical to perform and produces scientifically valid results. The biological response measurement must be sufficiently routine such that it is practical to perform...to obtain scientifically valid results. To meet this criterion, the biological response measurement must be adequately documented in scientific literature, must produce reproducible and verifiable results, and must have well defined and accepted statistical criteria for interpreting as well as rejecting results."

The DOI has identified [at 43 CFR § 11.62 (f)(4)] a number of biological responses which satisfy the above acceptance criteria. These include:

- Brain cholinesterase (ChE) enzyme activity
- Fish kills
- *In situ* bioassays
- Laboratory toxicity testing, including acute flow-through, acute static, partial-chronic (early life stage), and chronic (life cycle) toxicity tests
- Fin erosion
- Clinical behavioral signs of toxicity
- Avoidance responses
- Delta-aminolevulinic acid dehydratase (ALAD) inhibition
- Reduced fish reproduction
- Overt external malformations
- Skeletal deformities
- Internal whole organ and soft tissue malformation, and
- Histopathological lesions.

7.4.2 Description of Fishery Resources to be Assessed

Historically, the Clark Fork River and Silver Bow Creek have been contaminated with hazardous substances at concentrations sufficiently elevated to preclude most aquatic biota prior to 1973 (Johnson and Schmidt 1988; Knudson 1984), and water quality of Silver Bow Creek still is sufficiently contaminated to preclude the existence of fish populations (Camp Dresser & McKee 1991). In contrast, various species of trout and other non-game species have persisted in uncontaminated streams within the drainage (Camp Dresser & McKee 1991), and at least two species of native trout were reported in the area of Silver Bow Creek prior to the onset of mining in the 1800's (Knudson 1984).

Fish kills in the Clark Fork River have occurred frequently. Averett (1961) reported numerous fish kills in the Clark Fork between 1958 and 1960. Between 1983 and 1988 there were at least six documented fish kills, some killing several thousand fish (Johnson and Schmidt 1988). More recently, in July, 1991, there was a documented fish kill in the upper Clark Fork River caused by runoff from a slickens area (Phillips 1991).

Currently, the trout population which persists in the upper Clark Fork River between Warm Springs Ponds and Rock Creek is composed almost exclusively of brown trout (*Salmo trutta*) (Johnson and Schmidt 1988; Knudson 1984). Rainbow trout (*Oncorhynchus mykiss*) only occur infrequently above Rock Creek, over 100 river miles (160 km) below Warm Springs Ponds, while native bull (*Salvelinus confluentus*) and westslope cutthroat (*Salmo clarki*) trout have been virtually eliminated from the Clark Fork (Knudson 1984; Montana DNRC 1988). In contrast, these species are found in uncontaminated tributaries. For example, the

Blackfoot River supports populations of brown, rainbow, cutthroat, bull, and brook trout (*Salvelinus fontinalis*) (Knudson 1984) and German Gulch Creek support westslope cutthroat, brook, and brown trout (Camp Dresser & McKee 1991).

Knudson (1984) suggested that the Clark Fork River supports only three to 20 percent of its potential fish population. Brown trout densities near Deer Lodge, MT are less than 500 trout per mile, with densities decreasing to 50 trout per mile between Drummond and the confluence with Rock Creek (Johnson and Schmidt 1988; Workman 1985). In comparison, other large trout rivers in Montana support 2,000 to over 3,000 catchable trout (at least 7" in length) per mile (Knudson 1984).

In-stream bioassays for fish and invertebrates have been conducted in the Clark Fork River and Silver Bow Creek. These studies support the hypothesis that the cause of this reduced productivity is exposure to elevated concentrations of hazardous substances (Phillips and Spoon 1990; Johnson and Schmidt 1988). Mortality of rainbow trout fingerlings and fry in bioassays conducted in Silver Bow Creek was near 100% in studies conducted over the period 1986-1989. Significant mortality was also observed in the Clark Fork at Warm Springs, Deer Lodge, Gold Creek, and Beavertail (above Rock Creek) (Phillips and Spoon 1990).

7.4.3 Objectives of Research Plans

The overall objectives of the fisheries research plans are to:

- Determine that fishery resources of the Clark Fork Basin have been injured as a result of exposure to hazardous substances released from the four NPL sites, based on responses which meet DOI's acceptance criteria for biological resources; and
 - Quantify those injuries in terms of reductions in populations of brown and rainbow trout in Silver Bow Creek (Butte to Warm Springs Ponds) and the Clark Fork River (Warm Springs Ponds to Missoula) as compared to control sites.
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7.4.4 Research Plans

7.4.4.1 Injury Determination

Protocols for injury determination include the following:

- Fishery Protocol #1: Food-Chain Exposures [addresses biological responses *Death* -- 43 CFR § 11.62 (f)(4)(i), and *Behavioral Abnormalities* -- 43 CFR § 11.62 (f)(4)(iii).]
- Fishery Protocol #2: Physiological Impairment [addresses biological responses *Physiological Malfunctions* -- 43 CFR § (f)(4)(v), *Disease* -- 43 CFR § 11.62 (f)(4)(ii), and *Physical Deformations* -- 43 CFR § 11.62 (f)(4)(vi).]
- Fishery Protocol #3: Acute Toxicity in Pulse Events [addresses biological responses *Death* and *Physiological Malfunction* (reproduction).]
- Fishery Protocol #4: Behavioral Avoidance [addresses biological response *Behavioral Abnormalities*.]
- Fishery Protocol #5: Influence of Acclimation/Adaptation on Toxicity [addresses biological response *Death*.]

(1) *Food-Chain Exposures*

The principal objective of the Food-Chain Exposures protocol is to determine chronic toxicity to metals resulting from both water and food-chain routes of exposure in brown and rainbow trout. Two specific tasks will be performed:

Task 1: Determine acute and chronic toxicity and impaired growth in brown and rainbow trout exposed to different combinations of water/dietary exposure to metals.

Task 2: Identify behavioral abnormalities in exposed fish relative to control fish.

Methods:

Three test diets of forage invertebrates (i.e., trout prey species) were collected from the upper Clark Fork River in the summer of 1991. The collection sites were below Warm Springs Creek, below Gold Creek and above Turah Bridge. These sites were selected to represent a gradient in metals concentrations in forage invertebrates as the downstream distance increases from principal sources in Butte and Anaconda.

The three invertebrate diets were frozen immediately after collection. Each diet will be analyzed on a wet weight basis to determine the exact level of contamination. Diets will be prepared to eliminate disease potential from the food organisms, and to assure presence of the proper vitamins and minerals (Jackson SOP: F.P19⁵).

Diet samples will be stored for metal residue determination following NFCRC SOP C5.134. Samples will be acid digested prior to analysis with microwave heating according to NFCRC SOP C5.94. Residues of arsenic, cadmium, copper, lead, and zinc will be determined by atomic adsorption spectrophotometry following NFCRC SOPs C5.35, C5.33, C5.34, and C5.49, respectively. Analyses will be quality assured according to NFCRC SOP C5.135.

Test and control waters for the experiments will be formulated to simulate minimal pH, hardness, and alkalinity existing in the Clark Fork River during spring conditions (hardness = 100 mg/l; alkalinity = 100 mg/l; pH = 7.2-7.8).⁶ Test water will also contain a 1X concentration of metals, where X = 1.1 µg/L cadmium, 12 µg/L copper, 3.2 µg/L lead, and 50 µg/L zinc. The control water will contain no metals (0X). Test metals concentrations have been approved as being representative of environmental conditions in the Clark Fork River in joint meetings between USFWS, Montana DFWP, U.S. EPA, and ARCO (see Environmental Toxicology 1991 and NFCRC 1991). Test water will be prepared by addition of water of known hardness to control water produced by reverse osmosis and deionization. The test waters will be analyzed daily for hardness, alkalinity, conductivity, and pH, to ensure that the water quality is within 5% of the experimental design for those parameters.

Water will be sampled weekly from the 0X and 1X treatments throughout the 90 day experimental period to verify metals concentrations. All samples will be collected, filtered, and preserved according to NFCRC SOP C5.134. One hundred milliliters of each treatment water will be filtered using a Nalgene 300 filter holder. Each filtered sample will be transferred to a pre-cleaned, 125 ml I-Chem polyethylene bottle and preserved by addition of 1 ml Ultrex-II nitric acid. Dissolved cadmium, copper, lead, and zinc in these samples will be determined by graphite furnace atomic adsorption spectrophotometry according to NFCRC SOPs C5.40, C5.93, C5.38, and C5.97, respectively. Analyses will be quality assured in accordance with NFCRC SOP C5.135.

Eyed embryos of rainbow trout and brown trout were obtained in the fall of 1991 from the Ennis National Fish Hatchery in Montana and the Saratoga National Fish Hatchery in Wyoming. Eggs will be held in Heath® incubators until hatching. Temperature will be maintained at 10°C during holding and testing. Embryos, larvae, and juveniles will be

⁵ SOPs are contained within the Laboratory Analytical Protocol (LAP). See Appendix A for a description of the LAP.

⁶ mg/L = ppm; µg/L = ppb.

handled so as to minimize stress in accordance with the NFCRC-Columbia Animal Welfare Plan, and the USFWS Region 6 Fish Health Policy.

Task 1: Approximately 90 days after hatching, alevins will be exposed to either test or control water. Three dietary treatments (the invertebrates collected from below Warm Springs Creek, below Gold Creek, and above Turah Bridge) will be added to both the test and control exposures, resulting in a total of six treatment combinations of water and diet for each species.

Seventy-five newly hatched alevins will be placed in each experimental unit. Lengths, weights and metals residues (As, Cd, Cu, Pb, Zn) in fish will be measured at approximately 0, 20, 45, and 90 days. Experimental units will be checked daily for mortality.

Task 2: Behavior of fish in each of the 48 experimental units described above will be monitored bi-weekly by video to determine behavioral effects of water and dietary exposures. Differences in fish behavior will be evaluated as described in NFCRC SOP: B5.101.

(2) Physiological Impairment

The primary objective of this protocol is to identify physical deformations and physiological malfunctions in fish caused by chronic exposure to metals at concentrations typically found in Clark Fork River food and water.

This objective will be pursued in two tasks:

Task 1: Identify physiological malfunctions and physical deformations in fish sampled from Protocol #1 (Food-Chain Exposures) to correlate such malfunctions and deformations with trace metal exposures in water and diet.

Task 2: Identify physiological malfunctions and physical deformations in brown trout from the Clark Fork River based on those pathologies identified in Task 1.

Task 1: At the conclusion of the Food-Chain Exposures research, fish samples will be collected for physiological health measurements. The fish will not be fed for 24 hours prior to sampling to allow the gut to empty. Fish will be collected from each exposure for residue analyses of arsenic, cadmium, copper, lead, and zinc (UW SOP P.10 - P.14). Fish will be collected for lipid peroxidation, histological, stress protein and metallothionein analyses (UW SOP P.2 - P.6). Fish collected for metals analyses, stress protein and lipid peroxidation analyses will be weighed and placed in individual pre-labeled vials, frozen immediately in liquid nitrogen (UW SOP P.18), transported on dry ice, and stored at -70°C (UW SOP E.12) until analyzed. Fish collected for histological analyses will be fixed immediately in Bouin's Solution and stored in 50% ethanol until embedded.

Task 2: In the spring of 1992, brown trout will be collected from a control site and from three test sites in the Clark Fork River: below Warm Springs, below Gold Creek, and above Turah Bridge. Ten to twenty adult brown trout of mixed (but determined) sex will be collected from each sample site. Lengths and weights will be measured (UW SOP P.15) and an autopsy assessment will be performed on each fish (UW SOP P.1) in the field. Five of the brown trout from each site will be individually bagged and labeled, placed on dry ice, and stored for analysis. Whole body arsenic, cadmium, copper, lead, zinc, sodium, and calcium will be measured on these five fish (UW SOP P.7 and P.10 - P.14). Quality control will be conducted according to UW SOP P.8.

Ten of the brown trout will be dissected in the field. Sections of gill, liver, kidney, and intestine tissue approximately 500 mg in size (UW SOP P.29) will be collected from each fish, frozen immediately in liquid nitrogen and placed on dry ice (UW SOP P.18 and P.29). They will be stored at -70°C until they are processed and measured for lipid peroxidation and previously listed metals (UW SOP P.6). An additional section of fish tissue 200 mg in size will be taken, frozen and transported as described above, and analyzed for stress protein and metallothionein.

Additional fish will be collected from control and test sites for quality control analyses of the measurement procedures. Water samples from each of the field sites (control and test) will be collected for metal and anion measurements (UW SOP P.30, P.8, P.10-P.14). All of the above sampling procedures will follow UW SOP P.16 for sample numbering, tracing and reporting.

(3) Acute Toxicity in Pulse Events

The principal objective of this protocol is to determine the acute toxicity of pulsed concentrations of metal mixtures that occur in the Clark Fork River to brown and rainbow trout. This objective will be pursued in two tasks:

Task 1: Determine the relative sensitivity of early life stage and adult brown trout to pulsed metal exposures;

Task 2: Determine the relative sensitivity of brown trout fry from the Clark Fork and Big Hole Rivers, brown trout fry from a hatchery stock, and rainbow trout fry from a hatchery stock.

For Task 1, brown trout fry and adults will be obtained from a hatchery in Wyoming. For Task 2, brown trout eggs were obtained from spawning adults in the Clark Fork and Big Hole Rivers in November, 1991. The eggs and fry will be raised following UW SOP P.24.

Task 1: In the laboratory, fish will be held in waters representing a range of ambient conditions in the Clark Fork River (hardness = 100 to 200 mg/L; alkalinity = 100 to 200 mg/L; pH = 7.2 to 7.8) but with no metals. Fish will be acclimated to the glass test chambers for 24 hours, and then exposed to a two-hour pulse of cadmium, copper, lead and zinc. The relative concentrations of the metals in the simulated pulse will be based on the ratios of the metals measured during pulse events in the Clark Fork River, with the highest pulse concentration (" P_c ") based on the highest concentration measured during actual pulse events, as reported by the Montana DHES, DFWP, Montana State Bureau of Mines and Geology, and other sources.

Continuous-flow diluters (UW SOP P.28) will deliver a concentration equal to P_c , three 50% dilutions ($0.5P_c$, $0.25P_c$ and $0.125P_c$), and the control (no metals). There will be three replicates for each of these five treatments. During the two-hour pulse exposure and during a 96-hour post-exposure phase, mortality will be monitored at frequent intervals to determine time to death and overall mortality. Water chemistry parameters (pH, dissolved oxygen, hardness, alkalinity and temperature) will be monitored during all tests (UW SOP P.19-23).

During holding and laboratory acclimation periods fish will be fed 5% of body weight per day of a vitamin-fortified commercial trout diet. During the pulse experiments fish will not be fed. At the end of the tests, fish will be disposed of humanely (UW SOP P.26).

Task 2: Tests under Task 2 will be conducted exactly as specified in Task 1, above, except that the test fish will all be brown trout (Clark Fork River source, Big Hole River source, and hatchery source) and rainbow trout (hatchery source) hatched from eggs and tested at the fry stage.

(4) Behavioral Avoidance

The principal objective of this protocol is to identify avoidance behaviors in brown and rainbow trout when exposed to concentrations of metals representative of conditions found in the Clark Fork River. Rainbow and brown trout obtained from a hatchery source will be used for avoidance tests.

Avoidance tests will be conducted in accordance with NFCRC SOP B5.232. Tests will be conducted in a countercurrent-type avoidance chamber. This chamber is an 11 x 92 cm plexiglass cylinder in which water is received at both ends and exits through the center. Test or reference water can be supplied at either end. Fish response to water quality is determined by observing which end of the chamber is preferred.

Three specific tasks will be conducted:

Task 1: Avoidance tests will be performed with brown and rainbow trout using 0.1X, 0.5X, 1X, 2X, 4X, and 10X metals concentrations, where X is the same as in Protocol #1. Control water will be simulated Clark Fork River water without metals (0X).

Task 2: Avoidance tests will be performed with both brown and rainbow trout using a 1X metals concentration in waters of pH 5.0, 6.0, and 7.0. Control water will be simulated Clark Fork River water without metals (0X).

Task 3: Avoidance tests will be performed with rainbow trout acclimated to simulated tributary water. Control water for this test will be the simulated tributary water; test water will be simulated Clark Fork River water with 1X metals concentrations. Simulated tributaries will include soft water tributaries, medium-hard water tributaries, and hard water tributaries as described below:

- 1) Soft water tributary (e.g., Rock Creek): pH = 7, Hardness = 50, Alkalinity = 50, Conductivity = 60;
- 2) Medium hardness tributary (e.g., Little Blackfoot River): pH = 8, Hardness = 100, Alkalinity = 100, Conductivity = 150; and
- 3) Hard water tributary (e.g., Warm Springs Creek): pH = 8, Hardness = 200, Alkalinity = 200, Conductivity = 250.

Fish will be acclimated to and maintained in the control water for each task for a minimum of two weeks prior to testing. Fish behavioral responses will be observed at selected intervals for the duration of the test by counting fish in still frame pictures. Avoidance will be determined by the percent time or cumulative frequency in the metals exposure end of the chamber compared to the percent time in the control end of the chamber. Fish that are within the transition zone between the two ends during the observation time will be considered as position unchanged. Video equipment usage will be in accordance to NFCRC SOP F.E15.

Tests will be terminated and reinitiated if there is a disturbance to the avoidance apparatus, inconsistent water chemistry or temperature, disease, or aggression. The avoidance apparatus will be enclosed in a structure to shield against external disturbances (e.g., movement, sound, light). Control and test waters will be sampled daily to verify water quality parameters. All samples will be collected, filtered, and preserved according to NFCRC SOP C5.134. One hundred ml of each treatment water will be filtered using the Nalgene 300 filter holder. Each filtered sample will be transferred to a pre-cleaned, 125 ml I-Chem polyethylene bottle and preserved by addition of 1 ml Ultrex-II nitric acid. Determination of dissolved Cd, Cu, Pb, and Zn in these samples will be done by graphite furnace atomic absorption spectrophotometry according to NFCRC SOPs C5.40, C5.93,

C5.38, and C5.97, respectively. Analysis will be quality assured in accordance with NFCRC SOP C5.135.

(5) Influence of Acclimation/Adaptation on Toxicity

The principal objectives of this protocol are to determine whether differential sensitivity to metals toxicity exists between (1) brown and rainbow trout, and (2) resident brown trout in the Clark Fork River and control brown trout.

Juvenile fish will be used for all tests. Brown trout were obtained from the Clark Fork and Big Hole Rivers by collecting adult brown trout in November 1991, spawning them, and raising the eggs and fry (UW SOP P.24). Brown trout and rainbow trout also will be obtained from a hatchery source in Wyoming.

Control water will be formulated to simulate minimal spring conditions in the upper Clark Fork River as described in Protocol #1. Test water will be control water with added metal concentrations.

During holding and acclimation periods, fish will be fed 5% of body weight per day of a vitamin-fortified commercial trout diet. During toxicity tests fish will not be fed.

Task 1: Brown and rainbow trout juveniles from a hatchery stock and brown trout juveniles from the Clark Fork and Big Hole Rivers will be cold-branded to distinguish each group and acclimated to laboratory culture conditions for a minimum of two weeks (UW SOP P.24). At the start of each test exposure, fish will be divided into two groups. Control fish will be held in water comparable to Clark Fork River ambient conditions, but with no metals. Test fish will be held in water comparable to Clark Fork River ambient conditions with metals present at the 1X metal concentrations identified in Protocol #1.

After a three week period to allow physiological acclimation, a sample of each group will be exposed to a mixture of cadmium, copper, lead, and zinc. Exposure will continue for 96 hours with frequent monitoring of mortality to determine time to death and overall mortality. If results indicate that no acclimation occurred (e.g., no statistical difference in LT_{50} ⁷ between control and acclimated treatments within each of the three test groups), fish will be acclimated for an additional two weeks and then exposed in a similar manner. Water chemistry parameters (pH, dissolved oxygen, hardness, alkalinity and temperature) will be monitored during all tests (UW SOP P.19-23). At the end of the tests, fish will be disposed of humanely (UW SOP P.26).

⁷ The LT_{50} is defined as the time of exposure that is lethal to 50% of the test organisms.

Task 2: Brown and rainbow trout juveniles from a hatchery stock and brown trout juveniles from the Clark Fork River and the Big Hole River will be acclimated to laboratory culture conditions for a minimum of one month (UW SOP P.24). Each of the four groups of fish will then be used to determine an LC_{50} ⁸ dilution for an aqueous mixture of Cd, Cu, Pb and Zn. Water chemistry parameters (pH, dissolved oxygen, hardness, alkalinity and temperature) will be monitored during all tests (UW SOP P.19-23). At the end of the tests, fish will be disposed of humanely (UW SOP P.26).

7.4.4.2 Injury Quantification

The overall objective of the injury quantification phase is to compare trout populations in Silver Bow Creek (Butte to Warm Springs Ponds) and the Clark Fork River (Warm Springs Ponds to Missoula, henceforth "SBC/CFR") with those at control sites. Specific objectives of field sampling are as follows:

- To determine whether differences exist between the number, size and species of trout in SBC/CFR and control sites;
- To quantify differences in fish habitat in SBC/CFR and control streams in order to model available trout habitat.

Methods:

(1) Comparison of Trout Densities

Eighteen distinct reaches (discrete combinations of valley bottom type (VBT) and stream state) in SBC/CFR were identified using topographic and geologic maps, aerial photos, and subsequent ground-truthing. Control reaches with similar combinations of VBT and stream state corresponding to each of the SBC/CFR reaches subsequently were identified.

Trout population densities at all test and control reaches were sampled over the period July - October, 1991 using snorkeling and electrofishing techniques. Trout populations were measured at a total of four sampling sites within each reach by dividing each reach into 100 meter sections, then randomly selecting four of those sections for sampling. Fish habitat (including pool, riffle, run, etc.) was mapped at each site.

Fish densities were estimated by direct observation using snorkeling techniques (Hillman *et al.* In Press; Schill and Griffith 1984). A team of three to five observers maintained a

⁸ The LC_{50} is defined as the concentration of the contaminant that is lethal to 50% of the test organisms.

prescribed spacing from one another, with the number of observers and spacing based on water clarity. The prescribed spacing was maintained by grasping connected lengths of 3-cm-diameter polyvinyl chloride (PVC) pipe. Visibility was recorded as the maximum distance at which a two-inch fish could be recognized. Members of the team counted only those fish that passed below a lane between themselves and the observer to their left. The flexible PVC pipe enabled observers on each end of the counting lane to position themselves about one meter ahead of the others, facilitating the counting of any fish that move laterally along the counting lane. One observer moved upstream to count fish stationed close to each bank. Fish species, estimated length, and numbers were recorded at each sampling site, as were stream widths.

Electrofishing was used to 1) measure fish densities where snorkeling was not feasible, 2) validate the fish population estimates from the snorkeling, and 3) assess length/weight relationships for all trout collected. Biomass of trout in each sampling site was estimated with regression equations calculated from the length/weight relationships. A backpack or boat electrofisher was used, employing a three-pass, depletion method (Platts *et al.* 1983; Van Deventer and Platts 1989).

(2) Habitat Modeling

Trout habitat will be modeled using two methods. Macrohabitat features will be modeled using the Instream Flow Incremental Methodology (IFIM)(Bovee 1982). One of the four population sampling sites within each reach was randomly selected for IFIM measurements (depth, velocity, cover, substrate). Trout habitat suitability curves will be used in Physical Habitat Simulation (PHABSIM) models to calculate weighted usable area (WUA) (i.e., available habitat) per unit length of stream and per unit surface area. Trout populations (biomass and number of fish) in SBC/CFR and control sites will be normalized for available habitat.

A second approach will be used to permit evaluation of differences in microhabitat between SBC/CFR and control sites. Habitat measurements were performed at each of the population sampling sites using the transect methodology developed by Platts *et al.* (1983). Within each site, 28 to 30 transects were spaced 30 to 33 feet apart to measure a 1000-foot section. The parameters measured included: channel width, wetted perimeter width, riffle width, run width, pool width, pool rating, bank angle, average and thalweg depth, substrate, bank cover, vegetative overhang, canopy cover, bank alteration, organic debris, sun arc, and bank undercut. These data may be used in combination with PHABSIM to compare overall trout habitat at SBC/CFR and control sites.

7.5 GEOLOGIC RESOURCES: SEDIMENTS

7.5.1 Definition of Injury

Relevant definitions of injury for affected sediments in the Clark Fork Basin include:

- Concentrations of substances on bed, bank, or shoreline sediments sufficient to cause the sediment to exhibit characteristics identified under or listed pursuant to section 3001 of the Solid Waste Disposal Act, 42 U.S.C. 6921 [43 CFR § 11.62 (e)(1)];
- Concentrations of substances sufficient to have caused injury to groundwater [43 CFR § 11.62 (e)(8)]; and
- Concentrations of substances sufficient to cause injury ... to surface water, groundwater, air, or biological resources when exposed to the substances [43 CFR § 11.62 (e)(11).

7.5.2 Description of Sediment Resources to be Assessed

As described in Section 6.3, bed sediments of Silver Bow Creek from Butte to Warm Springs Ponds, the Warm Springs Ponds, and the Clark Fork River from Warm Springs Ponds to Missoula contain significantly elevated concentrations of hazardous substances relative to background, or control areas. The State's assessment of injury to sediment resources will concentrate on those areas of greatest injury to sediment resources attributable to releases of hazardous substances from the four NPL sites, and on those areas within which gross injury to sediment resources may contribute significantly to injury to aquatic life.

7.5.3 Objectives

The overall objectives of the sediment sampling plan are to determine the extent to which bed sediments of Silver Bow Creek, the Warm Springs Ponds, and the Clark Fork River have been injured by hazardous substances released from the four NPL sites. Specific objectives include:

- Characterize baseline concentrations of hazardous substances in sediments using control sites;
 - Determine concentrations of hazardous substances in SBC/CFR sediments;
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- Determine injury by comparing concentrations of hazardous substances in SBC/CFR sediments to control areas, using criteria identified in Section 7.5.1; and
 - Quantify injury to sediments by estimating the areal extent of injured sediments.

7.5.4 Research Plan

Sampling was conducted during the months of October and November, 1991 on Silver Bow Creek, the Clark Fork River, and principal tributaries of the Clark Fork River (Little Blackfoot River, Flint Creek, Gold Creek, and Rock Creek). Sampling sites along SBC/CFR were located at approximately 10 km intervals. At the mouths of the Little Blackfoot River, Flint Creek, Gold Creek and Rock Creek, three samples were taken both above and below the tributary to establish the effects of the tributaries on the Clark Fork sediment. In addition, samples were collected at each of the fisheries habitat sites (test and control) described in Section 7.4.4.2, above.

At each site, sediment was scraped from surface channel deposits in slack water areas using a polypropylene scoop and immediately wet-sieved in ambient river water through a 63 μ m polypropylene mesh sieve (U.S. Standard Sieve Mesh #230), into acid-washed, 250 ml, wide-mouthed, plastic bottles (Axtmann and Luoma 1991; Brook and Moore 1988). Samples were composited from a 20 m river reach. Co-located triplicate samples were collected at one site on each tributary and fishery control reach and one triplicate was collected at approximately every 10 sites on the main stem of the Clark Fork River and Silver Bow Creek.

Samples subsequently were transported on ice for preparation and analysis. Sediment slurries in the 250 ml sample bottles were centrifuged for 10 minutes at 2000 rpm and the supernatant discarded. The remaining sediment cake was dried in the same bottle for 24 hrs at 70°C, or until the sample weight had stabilized.

When analyzed, the dried sample will be ground by hand. Sub-samples of 0.5 g will be weighed for digestion after sitting in a desiccator for at least 24 hrs. Sediment digestion will be by a modified "aqua regia digestion" method recommended by U.S. EPA (Plumb 1981). The 0.5 g sub-sample will be placed into a teflon screw top microwave reaction vessel. Ten ml of freshly made aqua regia will be added to each reaction vessel. Samples will be allowed to pre-digest at room temperature for at least one hour, with vessel covers loosely affixed. The vessels then will be sealed and placed into a plastic container on a rotating carousel for heating in a microwave oven. After heating, the sample vessels will be removed from the oven and allowed to cool to room temperature. Once cool, the vessels will be removed from the plastic container, the lids removed and the digested samples filtered through 0.45 μ m

cellulose membrane filters and diluted to a final volume of 50 ml with "Milli-Q" deionized water.

Digestion solutions will be analyzed by Inductively Coupled Argon Plasma Emission Spectrometry (ICAPES) using a Jarrel-Ash Model 800 Atom Comp ICAPES, following manufacturer-recommended procedures. Analyses will be determined for As, Cd, Cu, Fe, Mn, Pb, and Zn. Major elements (e.g., Al, Ca, Mg, Na, and Ti) also will be analyzed by ICAPES to better characterize and compare sediment samples. Total carbon and carbonate carbon will be determined by coulometric methods; organic carbon will be determined by difference (Coulometrics, Inc. 1990; UIC 1987,1988).

7.6 GROUNDWATER RESOURCES

7.6.1 Definition of Injury

Relevant definitions of injury to groundwater resources of the Clark Fork River Basin include:

- Concentrations and duration of substances in excess of drinking water standards as established by sections 1411-1416 of the Safe Drinking Water Act (SDWA), or by other Federal or State laws or regulations that establish such standards for drinking water, in groundwater that was potable before the discharge or release [43 CFR § 11.62 (c)(1)(i)];
- Concentrations and duration of substances in excess of water quality criteria established by section 1401(1)(D) of SDWA, or by other Federal or State laws or regulations that establish such criteria for public water supplies, in groundwater that before the...release met the criteria and is a committed use [43 CFR § 11.62 (c)(1)(ii)];
- Concentrations and duration of substances in excess of applicable water quality criteria established by section 304(a)(1) of the Clean Water Act (CWA), or by other Federal or State laws or regulations that establish such criteria, in groundwater that before the discharge or release met the criteria and is a committed use as habitat for aquatic life, water supply, or recreation. The most stringent criterion applies when surface water is used for more than one of these purposes [43 CFR § 11.62 (c)(1)(iii)];
- Concentrations and duration of substances sufficient to have caused injury to other resources when exposed to groundwater [43 CFR § 11.62 (c)(1)(iv)].

7.6.2 Description of Groundwater Resources to be Assessed

Section 6.4 provided examples of data demonstrating exposure of groundwater resources in aquifers in the Butte, Montana Pole, Anaconda, and Milltown areas. The State intends to focus its assessment of injury to groundwater on these four areas, as well as examining existing data on groundwater recharge to SBC/CFR. Limited field sampling will be conducted to document pre-disturbance conditions in a control area.

7.6.3 Objectives of Research Plan

Objectives of the groundwater plan include the following:

- Identify controls in order to quantify baseline concentrations of hazardous substances;
- Quantify baseline concentrations of hazardous substances;
- Determine injury to groundwater based on criteria in Section 7.6.1; and
- Quantify injury to groundwater by estimating the areal and/or volumetric extent of injury.

7.6.4 Research Plan

It is anticipated that determination and quantification of injury to groundwater resources will rely primarily on existing literature containing information on the nature and extent of wastes, the levels of contamination observed in the groundwater resource, and groundwater conditions in control areas.

Control areas for potentially injured groundwater resources will be selected "...based upon their similarity to the assessment area and the lack of exposure to the contaminant releases" [43 CFR § 11.72 (d)]. In addition to using existing data on control areas, field sampling will be performed in the Thompson Park area south of Butte. This area is underlain by an extensive molybdenum-sulfide ore body containing areas of significant pyrite mineralization similar to the Butte Mining District and thus is a control site for the Butte Area.

Thompson Park Study

The objective of the sampling at Thompson Park is to characterized baseline groundwater quality for the Butte area. Samples will be analyzed for total and dissolved As, Cd, Cu, Fe, Mn, Mo, Pb, and Zn. In addition, Ca, Mg, Na, K, Cl, SO₄, HCO₃, and CO₃ will be analyzed to aid in the interpretation of the metals data.

Samples will be obtained up-gradient, adjacent to, and down-gradient of the molybdenite-sulfide orebody located at Thompson Park. Groundwater samples will be taken from existing wells within both the alluvial and bedrock aquifers. In addition, surface water samples may be taken from upper Blacktail Creek during base-flow (i.e., when the surface water flow is comprised entirely of groundwater from the alluvial aquifer).

Field sampling will be conducted a minimum of two times: during low-flow (baseflow) conditions, and during high-flow conditions. All sampling will be conducted using generally accepted methods, including methods included in the *Clark Fork River Superfund Site Investigations Standard Operating Field Procedures (SOPs), Draft (ARCO, September 1991)(CFRSSISOP)*. Stream samples will be collected per CFRSSISOP SW-1. Streamflow will be measured per CFRSSISOP SW-6. When collecting groundwater samples, the well will be purged until constant conditions of pH and conductivity are reached, at which time samples will be collected. A minimum of three casing volumes will be evacuated before sampling, which equals or exceeds the generally-accepted practice of three casing volumes as described in CFRSSISOP GW-1.

Other field data which will be collected includes:

- Specific conductivity (CFRSSISOP HG-6),
- pH (CFRSSISOP HG-5),
- Air temperature (CFRSSISOP HG-7),
- Water temperature (CFRSSISOP HG-7),
- Redox potential (CFRSSISOP HG-5),
- Static water level (CFRSSISOP GW-5), and
- Drawdown, pump discharge and pumping duration (CFRSSISOP GW-1).

8.0 LITERATURE CITED

AIRS. 1991. U.S. EPA Database. Office of Air Quality Planning and Standards. Research Triangle Park, NC.

Alloway, B.J. 1990. *Heavy Metals in Soils*. John Wiley & Sons, Inc, New York, 339 pp.

Averett, R.C. 1961. Macro-invertebrates of the Clark Fork River, Montana: A pollution survey. Prepared by Montana Board of Health and Montana Department of Fish and Game. Helena, MT. Water Pollution Control Report # 61-1. 27 pp.

Axtmann, E.V. and S.N. Luoma. 1991. Large-scale distribution of metal contamination in the fine-grained sediments of the Clark Fork River, Montana, U.S.A. *Appl. Geochem.* 6: 75-88.

Bovee, K.D. 1982. A guide to stream habitat analysis using the Instream Flow Incremental Methodology. Instream Flow Paper No. 12. U.S. Fish and Wildlife Service, Ft. Collins, CO.

Brook, E.J. and J.N. Moore. 1988. Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in bed sediment from the Clark Fork River, Montana (U.S.A.). *Science Tot. Environ.* 76: 247-266.

Brooks, R. 1988. Distribution and concentration of metals in sediments and water of the Clark Fork River floodplain, Montana. M.S. Thesis, University of Montana, Missoula, MT. 105 pp.

Camp Dresser & McKee (CDM). 1988. Preliminary analysis of aqueous geochemistry in the Berkeley Pit. Draft report to the Environmental Protection Agency. Helena, Montana. (As cited in Johnson & Schmidt 1988).

Camp Dresser & McKee (CDM). 1989. Final draft work plan for the Montana Pole NPL Site, Volume 1. Prepared for Montana Department of Health and Environmental Sciences.

Camp Dresser & McKee (CDM). 1990a. Final work plan for Remedial Investigation/Feasibility Study - Butte Mine Flooding Operable Unit. Prepared for the U.S. EPA, Helena, MT. Contract # 68-W9-0021.

Camp Dresser & McKee (CDM). 1990b. Revised final Remedial Investigation and Feasibility Study workplan: Milltown Reservoir Sediment Site. Prepared for Science Applications International Corporation, Helena, MT under U.S. EPA Technical Enforcement Support Contract.

Camp Dresser & McKee (CDM). 1990c. Preliminary endangerment assessment: Montana Pole NPL Site. Prepared for Montana Department of Health and Environmental Sciences, Helena, MT.

Camp Dresser & McKee (CDM). 1991. Preliminary baseline risk assessment, Lower Area One (LAO) Operable Unit, Silver Bow Creek. Prepared by Camp, Dresser, and McKee for U.S. EPA, Region VIII, Helena, MT.

CH₂M Hill Inc. and Chen-Northern Inc. 1989. Final public health and environmental assessment, data summary report. Rocker and Ramsay areas, Silver Bow Creek CERCLA Site, Montana. Prepared for Montana Department of Health and Environmental Sciences. Helena, MT.

CH₂M Hill Inc. and Chen-Northern Inc. 1990. Draft final, Silver Bow Creek CERCLA Site Phase II RI Data Summary, Vol. I: Report. Prepared for Montana Department of Health and Environmental Sciences, Helena, MT.

CH₂M Hill Inc., Chen-Northern and MSU Reclamation Research Unit. 1991. Draft final: Upper Clark Fork River Screening Study. 3 Volumes. Prepared for Montana Department of Health and Environmental Sciences, Helena, MT. Document #SBC-CFR-SST-D-R1-022891.

Coulometrics Inc. 1990. Instrumentation manual, model 5010 carbon dioxide coulometer. Golden, Colorado.

Duaime, T.E., R.A. Appleman, M.R. Miller, and J.L. Sonderegger. 1989. Final Report: Travona Mine Aquifer Test, Part I: Summary, water quality monitoring, sampling and results. Montana Bureau of Mines and Geology Open-File Report 218. 114 pp.

Duaime, T.E., J.L. Sonderegger and M. Zakuski. 1985. Hydrogeology of the Colorado Tailings area, Butte, Montana. In C.E. Carlson and L.L. Bahls, eds., *Proceedings of the Clark Fork River Symposium*. Montana College of Mineral Science and Technology, Butte, MT, pp. 4-20.

ENSR. 1989. Final Draft: Milltown Reservoir Sediments Site hydrogeologic investigations: Sampling and analysis plan. Prepared by ENSR Consulting and Engineering for Holland and Hart Attorneys at Law, Billings, MT.

Environmental Toxicology. 1991. Ecological risk assessment work plan: Milltown Reservoir Sediments Site baseline risk assessment. Prepared for U.S. EPA, Region VIII, Helena, MT. 100 pp.

Harkins, W.D. and R.E. Swain. 1907. Papers on smelter smoke: The determination of arsenic and other constituents of smelter smoke, with a study of the effects of high stacks and large condensing flues. *J. Amer. Chem. Soc.* 29: 970-998.

Hillman, T.W. J.W. Mullan, and J.S. Griffith. In Press. Accuracy of underwater counts of juvenile chinook and coho salmon and steelhead. *N. Amer. J. Fish. Manage.*

Ingman, G. L. and M. A. Kerr. 1990. Water quality in the Clark Fork River Basin, Montana; State Fiscal Years 1988-1989. Prepared for Montana Department of Health & Environmental Sciences, Helena, MT.

Johnson, H. E. and C. L. Schmidt. 1988. Clark Fork Basin Project: Status report and action plan. Prepared for the Office of the Governor, Helena, Montana.

Keystone. 1991. Preliminary draft, remedial investigation report, Montana Pole and Treatment Plant Site, Butte, Montana. Prepared by Keystone Environmental Resources for ARCO.

Knudson, K. 1984. A preliminary assessment of the impacts to the trout fishery - Upper Clark Fork River, Montana. Prepared for Montana Department of Fish, Wildlife, and Parks, Helena, MT. 30 pp.

Montana Board of Health. 1962. A study of air pollution in Montana, July 1961 - July 1962. Helena, Montana. (*As cited in Wake 1972.*)

Montana DHES. 1986. Water quality metals data, FY 1985, Clark Fork Basin, Appendix A. Prepared by the Montana Department of Health and Environmental Science - Water Quality Bureau.

Montana DNRC. 1988. Upper Clark Fork Basin: Water reservation applications. Draft Environmental Impact Statement for water reservation applications. Prepared by Montana Department of Natural Resources and Conservation. 171 pp.

Montana NRDP. 1991. Preassessment screen. Clark Fork River Basin NPL sites, Montana. Prepared by the Montana Natural Resource Damage Program, Helena, MT.

Montana Power Co. 1987. Milltown Dam rehabilitation Phase I evaluation of water quality monitoring data and Phase II construction dewatering and debris disposal. Butte, Montana. (*As cited in Johnson and Schmidt 1988.*)

Moore, J. N. 1985. Source of metal contamination in Milltown Reservoir, Montana: an interpretation based on Clark Fork River bank sediment. Report prepared for U.S. EPA, Helena, MT, 60 pp.

MultiTech. 1987. Silver Bow Creek: Warm Springs Ponds Investigation. Silver Bow Creek Remedial Investigation Final Report, Appendix C, Part 1. Prepared for Montana Department of Health and Environmental Sciences, Helena, MT.

Munshower, F.F. 1977. Cadmium accumulation in plants and animals of polluted and non-polluted grasslands. *J. Environ. Qual.* 6(4): 411-413.

NFCRC. 1991. Quality assurance plan - Milltown Endangerment Assessment Project: Assessing the effects of metals-contaminated sediment, water, and food chain on the fishery of the upper Clark Fork River, Montana. Prepared by the U.S. Fish & Wildlife Service - National Fisheries Contaminant Research Center, Columbia, Missouri, for the U.S. Environmental Protection Agency, Helena, MT. Approved June 24, 1991.

Peckham, A.E. 1979. Metals assessment of Silver Bow Creek between Butte and Gregson, Montana. Prepared by National Enforcement Investigations Center, Denver, CO, June 1979. 32 pp.

Phillips, G. 1984. Results of copper and cadmium analyses in gill tissue of brown trout collected from the Warm Springs bridge area of the Clark Fork River one day after the 1984 fish kill. Internal memoranda, August 23 and September 5, 1984. Montana Department of Fish, Wildlife, and Parks, Helena, MT.

Phillips, G. 1985. Relationships between fish populations, metals concentrations, and stream discharge in the upper Clark Fork River. In C.E. Carlson and L.L. Bahls, eds., *Proceedings of the Clark Fork River Symposium*. Montana College of Mineral Science and Technology, Butte, MT, pp. 57-73.

Phillips, G. 1988. Data summary table, metals residues in fish collected from the Mill-Willow Bypass, May 27, 1988. Prepared for the Montana Department of Fish, Wildlife, and Parks, Helena, MT.

Phillips, G. 1989. Data summary tables, metals residues in brown trout killed in the Clark Fork River, July 12, 1989. Prepared for Montana Department of Fish, Wildlife, and Parks, Helena, MT.

Phillips, G. R. and R. Spoon. 1990. Ambient toxicity assessments of Clark Fork River water - Bioassays and metal residues in brown trout organs. In *Proceedings of the second Clark Fork River Symposium*. Montana College of Mineral Science and Technology, Butte, MT. In Press.

Phillips, G. 1991. Data summary table, results of analyses of brown trout and sculpin gill tissues in fish collected after fish kill, July 26, 1991. Prepared for the Montana Department of Fish, Wildlife, and Parks, Helena, MT.

Platts, W.S., W.F. Megahan, and G.W. Minshall. 1983. Methods of evaluating stream riparian and biotic conditions. USFS, Forest and Range Exp. Sta. Tech. Rpt. INT-138. 70pp.

Plumb, R.H. 1981. Procedure for handling and chemical analysis of sediment and water samples. Prepared by Great Lakes Laboratory, SUNY-Buffalo for the U.S. EPA/Corps of Engineers Committee on Criteria for Dredged and Fill Material. Technical Report EPA/CE-81-1.

PTI. 1990. Smelter Hill Remedial Investigation/Feasibility Study. Phytotoxicity, surface water, and ground water investigations data summary/validation/ utilization report. Vol. 1. Prepared by PTI Environmental Services for ARCO Coal Company, Denver, Colorado.

PTI. 1991. Preliminary site characterization information, Smelter Hill Remedial Investigation and Feasibility Study. Prepared by PTI Environmental Services for ARCO, Anaconda, Montana.

Ray, G.J. 1983. Toxic metal enrichments from mining and smelting operations in riverside sediments of the upper Clark Fork. M.S. Thesis, University of Montana. Missoula, MT. (*As cited in Johnson and Schmidt 1988*).

Rice, P. M. and G. J. Ray. 1985. Heavy metals in floodplain deposits along the Upper Clark Fork River. In C.E. Carlson and L.L. Bahls, eds., *Proceedings of the Clark Fork River Symposium*. Montana College of Mineral Science and Technology, Butte, MT, pp. 26-45.

Schill, D.J. and J.S. Griffith. 1984. Use of underwater observations to estimate cutthroat trout abundance in the Yellowstone River. *N. Amer. J. Fish. Manage.* 7: 117-122.

Taskey, R. D. 1972. Soil contamination at Anaconda, Montana: history and influence on plant growth. M.S. Thesis, University of Montana, Missoula, MT.

Tetra Tech. 1986. Anaconda Smelter RI/FS geochemistry report. Prepared for Anaconda Minerals Co. Bellevue, WA. (*As cited in Johnson and Schmidt 1988*).

Tetra Tech. 1987. Anaconda Smelter Remedial Investigation/Feasibility Study Draft Report including Appendices. Prepared for Anaconda Minerals Company. Bellevue, WA. Document Control No. TTB 173 D1. 217 pp.

Thornell, R.J. 1985. Assessment of the Colorado Tailings Pond contribution to the decreasing ground and surface water quality. Special student project. Montana Bureau of Mines and Geology, Montana College of Mineral Science and Technology. Butte, MT. (*As cited in Johnson and Schmidt 1988*).

UIC. 1988. Instruction manual, model 5120 total carbon apparatus. Joliet, IL.

-
- UIC. 1989. Instruction manual, model 5230 acidification module. Joilet, IL.
- U.S. EPA. 1972. A water quality study of the upper Clark Fork River and selected tributaries. Prepared by the U.S. EPA Region VIII, Helena, MT.
- U.S. EPA. 1990. Record of Decision: Silver Bow Creek/Butte Area NPL Site, Warm Springs Ponds Operable Unit. Upper Clark Fork River Basin, Montana.
- U.S. EPA and Montana DHES. 1990. Clark Fork Superfund Sites: Master Plan. Prepared by U.S. Environmental Protection Agency and Montana Department of Health and Environmental Sciences, Helena, MT.
- Van Deventer, J.S. and W.S. Platts. 1989. Microcomputer software system for generating population statistics from electrofishing data - user's guide for MicroFish 3.0. USDA Forest Service General Technical Report INT-254.
- Wake, B.F. 1972. Air Pollution in Montana. In R. Bigart, ed., *Environmental Pollution in Montana*. Mountain Press Publishing Co., Missoula, MT, pp. 23-38.
- Wells, A.E. 1920. Report of the Anaconda Smelter Smoke Commission covering the period from May 1, 1911 to October 1, 1920. J.H. Hammond, L.D. Ricketts, and V.H. Manning, Commissioners. Report to the Department of Justice. 135 pp. (*As cited in Taskey 1972*).
- Woessner, W. W., J.N. Moore, C. Johns, M.A. Popoff, L.C. Sartor and M.L. Sullivan. 1984. Final report: Arsenic source and water supply remedial action study, Milltown Montana. Prepared for Montana Department of Health and Environmental Sciences, Helena, MT. 448 pp.
- Workman, D. 1985. Trout Populations in the Clark Fork River, Warm Springs to Superior, Montana. In C.E. Carlson and L.L. Bahls, eds., *Proceedings of the Clark Fork River Symposium*. Montana College of Mineral Science and Technology, Butte, MT, pp. 156-161.
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APPENDIX A
QUALITY ASSURANCE PROJECT PLAN

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LIST OF ACRONYMS

AM	Assessment Manager
CC Blank	Continuing Calibration Blank
COC	Chain-of-Custody
DOI	U.S. Department of Interior
FTL	Field Team Leader
GFAA	Graphite Furnace Atomic Absorption
GPC	Gel Permeation Chromatography
IC Blank	Initial Calibration Blank
ICP	Inductively Coupled Plasma Emission Spectrometry System
IDL	Instrument Detection Limits
LAP	Laboratory Analytical Protocol
MSA	Method of Standard Additions
NIST	National Institute for Standards and Testing
NRDA	Natural Resource Damage Assessment
NRDP	Natural Resource Damage Program
PDL	Project Detection Limit
PM	Project Manager
QA	Quality Assurance
QAM	Quality Assurance Manager
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QAR	Quality Assurance Reviewer
QC	Quality Control
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
U.S. EPA	United States Environmental Protection Agency
USGS	United States Geological Survey

1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) describes the policies, procedures, specifications, standards, and documentation which will produce data that meet the objectives of the Clark Fork River Basin NPL Sites NRDA.

This QAPP addresses procedures to assure the sufficient precision, accuracy, completeness, representativeness and comparability of field and laboratory data generated in the assessment. It also provides a framework for evaluating existing data which may be used in the assessment. This QAPP establishes quality assurance goals for sample and data acquisition, handling, and assessment. It is intended to guide field, laboratory, review and assessment personnel in relevant aspects of data collection, assessment, management, and control.

Quality Assurance (QA) is an integrated program designed to assure reliability of monitoring and measurement data. Quality Control (QC) is the regular application of procedures for attaining goals in the monitoring and measurement process. Quality assurance procedures such as tracking, reviewing and auditing may be implemented as necessary to assure that all assessment work is performed in accordance with professional standards, U.S. Environmental Protection Agency (U.S. EPA) guidelines, and specific objectives stated in the Assessment Plan and this QAPP.

Quality control of sample collection, analysis and assessment will be performed by technical project personnel. Field and laboratory equipment will be maintained and calibrated, and records of these kept in accordance with procedures established by this QAPP. Quality control of project deliverables will be provided through technical and administrative staff review. Document control procedures will be implemented to track documents generated by this assessment, including research plans, field notes, chain-of-custody forms, laboratory data, and final reports. Laboratory methods will be documented in a Laboratory Analytical Protocol (LAP) which contains all standard operating procedures (SOPs) used for sample analysis. The LAP will be updated as methods and procedures are reviewed and accepted for use.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The QA/QC project organization is shown in Figure A-1. Primary responsibility for implementing this QAPP and its supporting documents rests with the Assessment Manager (AM), the Quality Assurance Manager (QAM) and the Quality Assurance Reviewer (QAR). Project Managers (PM) submit research protocols, which are subsequently reviewed by the AM, QAM and QAR for consistency with and adherence to this QAPP.

The Field Team Leader (FTL) assures that field staff follow the guidance spelled out in this document and other referenced documents, as well as in project-specific methods. The FTL will note significant deviations in QC, sample integrity, the operation of field equipment, and the recording of field data. Upon discovery of significant deviations that could compromise the integrity of results, the FTL will report the such deviations to the PM. Significant deviations will be recorded in the field logbook, and will be reported by the FTL to the PM at the end of each field trip. The FTL or another person specifically designated is also responsible for sample custody until custody is relinquished to the laboratory Quality Assurance Officer (QAO).

A QAO at each laboratory will assure that appropriate procedures are followed during sample analysis. The QAO is responsible for sample receipt and storage, maintaining data and document storage files, documenting modifications from standard procedures, and laboratory QA/QC requirements.

Significant deviations from this QAPP found by the FTL or the QAO will be reported to the PM. The PM will then report to the AM in a timely fashion. The AM, in consultation with the QAM and QAR, will propose any corrective actions, which will be relayed to the PM. It is the responsibility of the PM to finalize and implement the corrective action. A summary of significant deviations and any corrective actions will be included in the final project report to the Montana Natural Resource Damage Program (NRDP).

Field and laboratory data will be reviewed according to guidance specified in Sections 10.3 and 11.0. The purpose of this review is to assure that data generated in this assessment are of sufficient quality to meet project objectives.

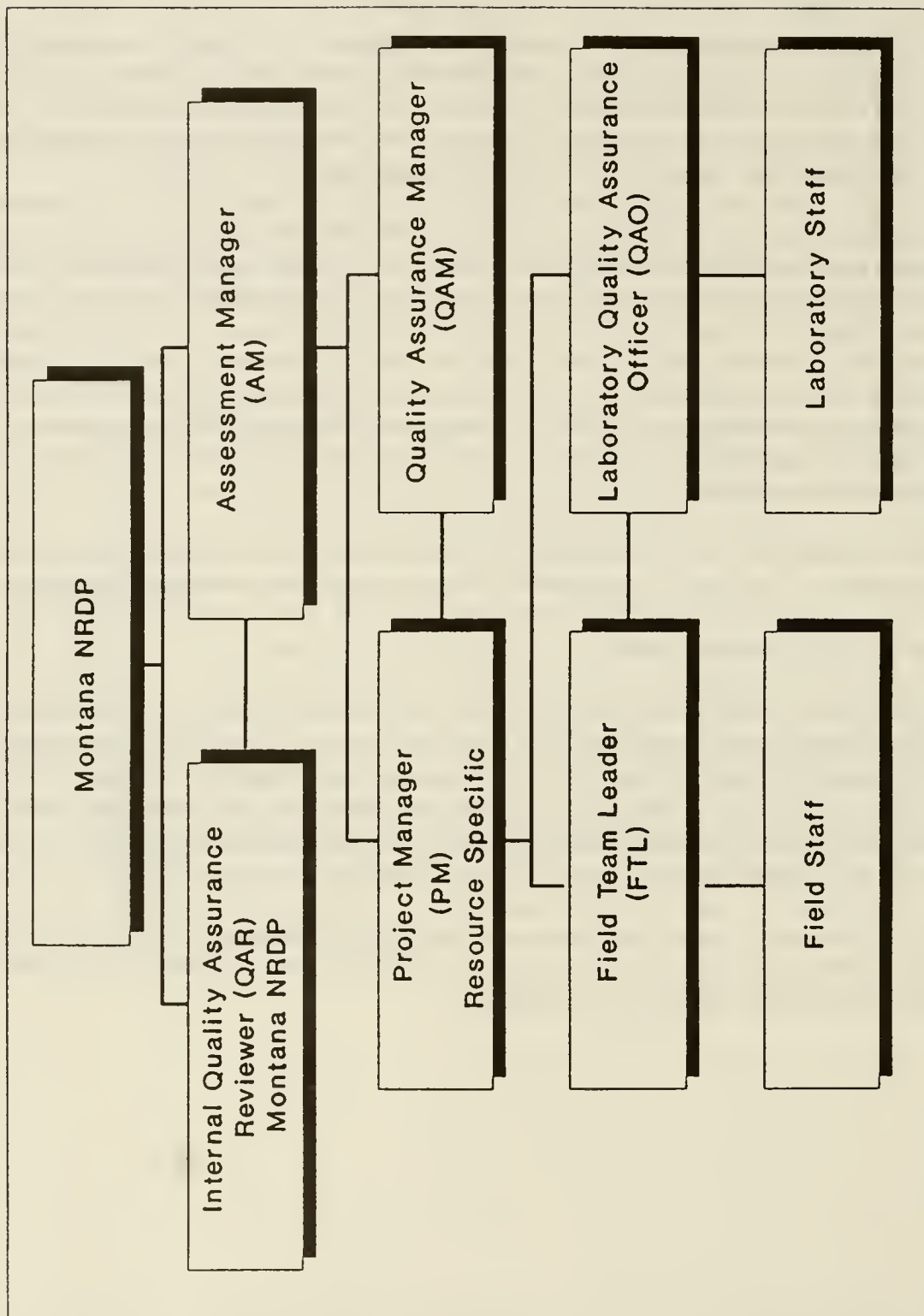


Figure A-1. Clark Fork Damage Assessment QA/QC Organizational Chart

3.0 OVERVIEW OF QA/QC TARGETS FOR CHEMICAL DATA

Quality Assurance targets for analytical data are based on the intended uses of the data, as stated in the objectives of the various research protocols included in the Assessment Plan. QA/QC targets are specified in Section 4.0. QC target limits (Table A-4) may be re-assessed in light of the actual error levels obtained.

QA objectives are defined as follows:

- Precision - a measure of mutual agreement among individual measurements of the same analyte, usually under prescribed similar conditions. Precision usually is expressed in terms of the relative percent difference (RPD) between measurements.
 - Accuracy - the degree of agreement of a measurement (or an average of measurements of the same parameter), X , with an accepted reference or true value, T , usually expressed as the difference between two values, $X-T$, or the difference as a percentage of the reference or true value, $100 (X-T)/T$, and sometimes expressed as a ratio, X/T . Accuracy is a measure of the bias in a system.
 - Completeness - a measure of the total number of samples or data points obtained compared to the total number proposed.
 - Representativeness - expresses the degree to which data accurately and precisely represent a characteristic of a population or an environmental condition.
 - Comparability - expresses the confidence with which one data set can be compared to another.
-

4.0 DATA QUALITY OBJECTIVES

Data quality objectives for this assessment are summarized in Tables A-1 through A-4. Detection limits for metals are presented in Table A-1. Precision, accuracy, and completeness goals are given in Table A-2. Containers, preservation methods and holding times are summarized in Table A-3. Table A-4 summarizes the target QC criteria for laboratory analysis of metals in various media. Data will be assessed during the data validation phase using the goals presented in Tables A-1 through A-4, and limitations with respect to project objectives will be noted.

Data usability for the assessment will be as follows:

- Data which meet QC targets will be considered to be usable.
 - Data which do not meet QC targets but can be justified in terms of complex matrices or by means of statistical review will be considered to be usable.
 - Data which have limited QC (i.e., calibrations and instrument checks) and/or are analyzed in the field may be considered to be usable for certain project objectives, and will be considered usable for screening and presence/absence determinations.
 - Data with little or no QC may be considered usable for certain project objectives.
-

Table A-1
Inorganic Target Analyte List (TAL)

Analyte	Project Detection Limit (ppb)
Aluminum	200
Arsenic	30
Barium	200
Beryllium	5
Cadmium	20
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	35
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	30
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20

TABLE A-2
DATA QUALITY OBJECTIVES FOR PRECISION,
ACCURACY, AND COMPLETENESS

Analyte	Matrix	Units	Accuracy (%)	Precision (%)	Completeness (%)
Ag, As, Be, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Zn	Soils, sediments, and tailings	mg/kg (ppm)	50	50	95
As, Cd, Cu, Pb, Zn	Plant tissue	mg/kg (ppm)	50	50	95
Ag, As, Be, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Zn	Groundwater and surface water	mg/l (ppm)	25	25	95
Total organic carbon (as carbon)	Soils, sediments, tailings	mg/kg (ppm)	35	35	95
Total sulfate	Groundwater and surface water	mg/l (ppm)	25	20	95
Chloride	Groundwater and surface water	mg/l (ppm)	25	20	95

TABLE A-3
CONTAINERS, PRESERVATION TECHNIQUES,
AND HOLDING TIMES

Parameters	Container	Preservative	Maximum Holding Time
Specific electrical conductivity	P,G	Cool, 4°C	28 days
pH	P,G	None required	Analyze immediately
Dissolved oxygen (DO)	G bottle and top	None required	Analyze immediately
Temperature	P,G	None required	Analyze immediately
Eh	P,G	None required	Analyze immediately
Bicarbonate (HCO ₃) and carbonate (CO ₃)	P,G	Cool, 4°C	14 days
Sulfate (SO ₄)	P,G	Cool, 4°C	28 days
Chloride (Cl)	P,G	None required	28 days
Metals: Ag, As, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Zn	P,G	HNO ₃ to pH <2	6 months
Mercury (Hg)	P,G	HNO ₃ to pH <2	28 days

TABLE A-4
TARGET QC CRITERIA FOR LABORATORY ANALYSIS OF METALS IN VARIOUS MEDIA¹

Water and Soil Samples	
QC Item	QC Limits
Initial Calibration (IC) (GFAA: 3 to 5 point)	$r < .995$ Daily
IC ICP 1 point	90-110 %R/Daily
Continuing Calibration (CC) (check standard)	90-110 %R 1/20 samples
IC or CC blank	$< \text{PDL}$ (absolute value), or $2x \text{IDL}$, whichever is less 1/20 samples
Preparation (method) blank	$< \text{PDL}$ 1/20 samples
Spike	50-150 %R 1/20 samples
Duplicate	$< 35 \% \text{RPD}$ $\pm 2x \text{PDL}$ (if value $< 5x \text{PDL}$) 1/20 samples
Serial dilution ICP	$\pm 15\%$ if sample result $> 50x \text{IDL}$ optional
ICP interference check sample	$\pm 25\%$ 1 per 8 hours
Laboratory control sample	$\pm 20\%$ water 1/50 samples or 1 per collection period (if available) soil - U.S. EPA limit
GFAA: duplicate injections	$\text{RSD} \pm 20\%$ each sample
Analytical spike GFAA	85-115 %R or go directly to MSA: reference CLP decision tree
MSA - 3 spikes (GFAA)	$r < .995$
Method detection limit	$\leq \text{PDL}$
Fish and Animal Tissue - Recommended Same as above with the following exceptions	
Gel Permeation Chromatography (GPC) cleanup	recommended
Duplicate	$< 50\% \text{RPD}$, $2x \text{PDL}$
Analytical spike	may be expanded
MSA - 3 spikes	may be expanded

¹ See Table A-2 for specific media.

5.0 QUALITY CONTROL PROCEDURES FOR FIELD SAMPLING AND MEASUREMENTS

The objectives of sampling procedures and field measurements are to obtain samples and measurements which are representative of the resource being investigated. Sample contamination is prevented by using experienced field personnel, good sampling techniques, proper sampling equipment and equipment decontamination procedures.

Field measurements and sampling will be performed in accordance with DOI NRDA regulations, as appropriate. When sampling methodologies are not specified in the regulations, sampling will be conducted using generally accepted methods as approved by the QAR.

Field QC samples will be used to evaluate overall field and analytical variability. Objectives for precision and accuracy (Table A-2) will be achieved in two ways: (1) field duplicate and/or split samples will be collected, when appropriate for the media being sampled and the sample collection method; and (2) matrix spike and matrix duplicates will be analyzed by the laboratory. Field variability is measured by the field duplicates' relative percent difference (RPD). Sampling precision is measured by the field splits' RPD. The accuracy of laboratory methods is measured by matrix spikes' percent recovery. The precision of laboratory methods is measured by laboratory duplicates' RPD.

The following field QC sample collection and analysis frequencies will be considered as appropriate targets for the purposes of this assessment:

- Field split samples at a frequency of 1 in 20;
- Field duplicate samples at a frequency of 1 in 20;
- Field blanks (trip, decontamination, cross-contamination) at a frequency of 1 in 20 samples, once per sampling event, or once per change in equipment, whichever is most frequent; and
- Bottle blanks at a frequency of 1 per bottle lot.

The frequency which yields the greatest number of QC samples will be used, i.e., one per matrix, one per twenty samples, or one per trip.

A field logbook will be kept of field data, observations, field equipment calibrations, samples and chain of custody. Entries will be made in waterproof ink. Mistakes will be lined out with a single line and initialed by the person making the correction. The logbook may contain the following information, as appropriate:

- Name of project or investigation,
 - Site name and number,
 - Sample numbers,
-

- Date and time of sampling,
 - Sample collectors' signatures or initials,
 - Results of instrument calibrations and field measurements,
 - Pertinent field observations, i.e., weather conditions, flow conditions, water clarity, unusual conditions, etc.,
 - QC samples which were collected,
 - Photographs,
 - Chain-of-custody information, and
 - Deviations from sampling plan.
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6.0 QUALITY CONTROL PROCEDURES FOR SAMPLE COLLECTION, HANDLING, AND PRESERVATION

Research protocols may describe or reference specific procedures, as appropriate, including:

- Collecting and compositing samples,
- Processing samples to assure proper subsampling, and
- Decontaminating sampling equipment prior to sampling and between each sampling event.

Sample containers will be kept closed until used. Samples will be labeled when they are collected and recorded in the field logbook along with other pertinent collection data.

Field replicates will be clearly identified and recorded. The following additional criteria will assure that data are representative of environmental conditions and are comparable to existing data:

- Samples will be of sufficient size to attain detection limits,
- All subsamples will be taken from well-homogenized composite samples,
- Collection procedures will follow appropriate methods to assure sample integrity,
- Samples will be isolated from cross contamination during sampling, and
- Field blanks will not be used for any of the lab QC samples.

Field sampling information will be recorded in the field logbook. Significant deviations from sampling procedures as described or referenced in the Assessment Plan will be documented in the field logbook.

Sample volumes will be based on standard analytical procedures. Prior to sampling, sample bottles will be rinsed with either sample or distilled water, as appropriate to the medium sampled. Bottles for metals analysis will be acid-soaked to remove any trace metal contaminants that may be adsorbed to the sides of the container. Samples will be preserved following U.S. EPA recommendations; all preservatives and bottle types will follow guidelines outlined in Table A-3. Certified grade reagents will be used. Cooling the samples to 4°C is recommended for a number of chemical constituents in water samples. In the field, this is accomplished by storing the samples on ice.

7.0 QUALITY CONTROL PROCEDURES FOR QUALITY CONTROL SAMPLES

The following types of QC samples may be collected in the field as part of a sampling program:

1. Bottle Blank

One bottle blank will be analyzed for each lot of bottles to verify that interior bottle surfaces are free of contamination. A deionized water rinse of a bottle will be collected for analysis after rinsing bottles three times with deionized water. Bottles which have been prepared (acid-soaked) for metals analyses should be tested after preparation. A trip blank may serve the purposes of a bottle blank. However, if a trip blank exhibits contamination, a bottle blank (using a bottle kept in reserve) should be run to determine the source of the contamination.

2. Trip Blank

Trip blanks measure potential sample contamination from the sample bottle, reagent water or preservative, or contamination from preparing, preserving, handling or transporting the blank from the field to the laboratory and back. The trip blank is prepared by filling a sample bottle with deionized water. It is transported in the sample shipping container to the field and remains unopened until preserved (if appropriate) in the field.

3. Decontamination Blank

A decontamination blank is prepared for analysis whenever there are changes in sample collection procedures, sample decontamination procedures, sampling equipment or sample collection personnel. This blank consists of deionized rinse water collected after decontaminating sampling equipment.

4. Field Cross-Contamination Blanks

These blanks consist of laboratory analytical-grade filter paper or kimwipe swipe samples of decontaminated sample-handling equipment (spatulas, augers, spoons, core-barrels, etc.).

5. Field Duplicates

Field duplicates are samples collected identically and consecutively over a minimum period of time. They provide a measure of the total field sampling and laboratory analytical bias, including bias resulting from the heterogeneity of the medium being sampled.

6. Field Split Samples

These samples are aliquots of sub-divided sample after appropriate mixing and homogenization have been performed. Split samples are prepared and analyzed when a field sample is collected as a composite sample and is subsampled prior to laboratory preparation and analysis. Emphasis will be placed on the homogeneity of split samples.

8.0 QUALITY CONTROL PROCEDURES FOR SAMPLE CUSTODY

8.1 DOCUMENTATION OF CHAIN-OF-CUSTODY

The documentation of a sample's history (from time of collection through sample analysis to final disposal) is referred to as "chain-of-custody" (COC). The components of the field COC (custody seals, field logbook, COC record, sample tags), laboratory COC (COC record, laboratory sample log-in/log-out logbook, laboratory sample storage records, laboratory sample disposal records), and procedures for their use are described in the following sections.

A sample is considered to be under a person's custody if it is: (1) in a person's physical possession, (2) in view of the person after he/she has taken possession, (3) secured by that person after being in his/her possession, or (4) in a designated secure area.

8.2 CHAIN-OF-CUSTODY RECORD

To establish the documentation necessary to trace sample possession from the time of collection, a COC record will be completed and accompany every sample. The COC record may contain the following information, as appropriate:

- Sample number (associated with a sampling location),
- Signature of sample collector,
- Date and time of collection,
- Sample tag number,
- Signatures of persons involved in the chain of possession, and
- Inclusive dates and times of possession.

In order to maintain COC, each person in custody of the sample will sign the form. Samples will not be left unattended unless placed in a secured and sealed container with the COC record inside the container.

8.3 SAMPLE TAGS

Sample tags will be affixed to sample containers at the time of sampling. Gummed paper labels or tags are adequate (indelible marking pens may also be used to record sample identification information directly on the sample container) and will include the following information, as appropriate:

- Sample number (tied to a sampling location);
 - Signature of collector;
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- Date and time of collection;
- Sample tag number, if any; and
- Preservation, if any.

8.4 CUSTODY SEALS

Custody seals are used to detect unauthorized tampering with samples after sample collection until the time of analysis. Gummed paper seals and custody tape may be used for this purpose. The seal will be attached so that it must be broken to open the sample container. Seals will be affixed to sample bottles before samples leave the custody of sampling personnel. Shipping containers will also contain seals to detect possible tampering.

8.5 LABORATORY CUSTODY

Laboratory custody may include, as appropriate:

- Designation of a sample custodian,
- Correct completion by the custodian of the COC record and analysis request sheet, including documentation of sample condition upon receipt, and
- Laboratory sample tracking and documentation procedures.

The sample will be delivered to the laboratory (accompanied by the COC record and an appropriate sample analysis request sheet), to a person in the laboratory authorized to receive samples. Samples will remain in an area into which access is limited to authorized personnel. Movement of samples out of and into the secure area for purposes of sample preparation, sample analysis, etc. will be recorded. This information will document dates and times of movement, persons handling samples, and the custody of samples when outside of the secure area.

9.0 QUALITY CONTROL PROCEDURES FOR SAMPLE ANALYSIS

Analytical methods will be consistent with or equivalent to U.S. EPA methods or some other commonly accepted or approved method, as approved by the QAM.

9.1 EQUIPMENT OPERATION, MAINTENANCE, CALIBRATION AND STANDARDIZATION

All field and laboratory equipment and instruments will be operated, maintained, calibrated and standardized in accordance with U.S. EPA-accepted or manufacturers' practices. Field and laboratory equipment and instrument SOPs may contain, as appropriate:

- Routine preventive maintenance procedures;
 - Calibration methods, frequencies, and description of calibration solutions;
 - Standardization procedures; and
 - Precision and accuracy assessment procedures.
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10.0 INTERNAL QUALITY CONTROL

Internal quality control procedures assure the consistency and continuity of data. Internal QC procedures may include:

- Instrument performance checks;
- Instrument calibration;
- Documentation of the traceability of instrument standards, samples and data;
- Documentation of analytical methodology and QC methodology; and
- Documentation of sample preservation and transport.

10.1 ANALYTICAL LABORATORY PROGRAM

Laboratory reagents will be reagent-grade or higher quality. Each new lot of reagents should be tested for quality, and results recorded to document test lots. Calibration standards and laboratory control samples will be traceable to the National Institute for Standards and Testing (NIST), the United States Geological Survey (USGS), the U.S. EPA, or other U.S. EPA-approved sources. Preparation and use of these samples will follow applicable U.S. EPA guidance.

A laboratory's analytical QC program will include the following types of QC samples, as appropriate to project objectives (Table A-4 summarizes the use, frequency, and QC limits for each sample type):

1. Analytical QC Samples

- a. Laboratory water will be tested to demonstrate that it is free of contaminants at levels above the detection limit for the applicable analytical procedure.

- b. **Method blank/reagent blank (preparation blank)**

A laboratory pure water blank is analyzed along with all samples submitted for analyses. The method blank is processed through all procedures, materials, and labware used for sample preparation and analysis. In cases of non-aqueous samples, reagent blanks serve as method blanks.

- c. **Calibration standards**

Three calibration standards will be used in generating a standard curve for analyses. After the Inductively Coupled Plasma Emission Spectroscopy System (ICP) is initially calibrated, only one standard (the initial calibration

verification standard) is required each day unless the instrument goes out of calibration. The graphite-furnace atomic absorption (GFAA) instrument generally will use a three point curve.

d. Continuing calibration standard (check standard)

A continuing calibration standard is prepared in the same manner as a calibration standard. It is used to validate an existing concentration calibration standard file. This standard can provide information on the accuracy of the analytical method and of instrument performance and response independent of sample matrix and preparation procedure.

e. Laboratory control sample

This is a sample of known value used to validate the analytical procedure. Control samples are used each time an analysis is made, and at a frequency of one for every 50 samples. For soils, the U.S. EPA has established guidance for the specific laboratory control sample of interest (see Table A-4). Comparable fish and plant tissue laboratory control samples have yet to be determined and may not be available.

f. Matrix spikes/analytical spikes

Three inorganic matrix/analytical spikes may be used to determine accuracy of the analytical method. These spikes are:

1. Matrix (predigest) spike - a sample is prepared in duplicate and a known spike solution containing pure analytes of concern is added to one of the duplicates before the sample is digested. This spike gives an indication of the effectiveness of the method in recovering the analytes of interest. It can also be a measure of the quality of laboratory techniques. Because the spike is a duplicate sample, it is affected by the homogeneity of the sample and sample preparation. It should be correlated to the duplicate RPD results. Percent recovery (%R) is calculated as:

$$\%R = 100(S-U)/T$$

Where S is the measured value of analyte after the spike is added, U is the measured value of analyte in the sample before the spike is added, and T is the value of the spike.

2. Post-digest spike - this is a known spike solution which is added to the digestate when the matrix spike does not meet QC limits. No limits have yet been established for this sample. Percent recovery is calculated as above.
3. Analytical spike - this spike is added after digestion to all samples which are to be analyzed by GFAA. The percent recovery for this spike is used to determine if the analysis is to be quantitated from the initial calibration curve or if the Method of Standard Additions (MSA) is to be used.

g. Laboratory Duplicate Sample

Aliquots (e.g., subsamples) are made in the laboratory of the same sample, and each aliquot is treated exactly the same throughout the analytical method. The relative percent difference (RPD) between the values of the duplicates, as calculated below, is a measure of the precision of the analytical method (RPD is calculated as an absolute value):

$$RPD = [(D_1 - D_2)/(D_1 + D_2)/2] \times 100$$

Where *RPD* is the relative percent difference, D_1 is the first sample value, and D_2 is the second sample value (duplicated).

2. Quality Control Check Samples

Quality control check samples will be used to evaluate analytical techniques and laboratory performance.

a. Initial and continuing calibration blanks

Initial calibration (IC) and continuing calibration (CC) blanks will consist of distilled water blanks analyzed at the beginning of each day and after every 20 samples to assure that carryover contamination does not occur. Negative blank values will be reported by the laboratory.

b. Interference check sample

The interference check sample for ICP analysis indicates the efficiency of the ICP in correcting for inter-element interferences.

c. Serial dilution sample

The ICP serial dilution sample monitors non-linear matrix interference.

10.2 QUALITY CONTROL PROCEDURES FOR FIELD SAMPLING AND MEASUREMENTS

Field QC will be assured through the analysis of duplicates and blanks. Field measurement QC will be assured through adherence to the Assessment Plan and procedures specified in this QAPP. QC checks may occur during field sampling and measurement, and will be the responsibility of the FTL. A performance (field) audit may occur during sampling to assure adherence to research protocols.

QC of field data will be accomplished by following equipment calibration procedures specified in the SOPs.

10.3 DATA REVIEW

Field and laboratory data will be reviewed as follows:

1. Data will be screened for inclusion and frequency of specific QC information (detection limit verification, initial calibration, continuing calibration, duplicates, spikes, reagent blanks, field blanks, etc.). Request for reanalysis or request for additional QC supporting information can be made at this point.
 2. QC supporting information will be screened for QC data outside established control limits. Request for reanalysis can be made at this point also.
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3. Measurement data will be reviewed in accordance with the procedures described below:
 - a. Representativeness
 - Comparing actual sampling procedures to those described in the Assessment Plan,
 - Examining the results of QC blanks for external sample contamination,
 - Identifying non-representative data or data to be classified as questionable.
 - b. Accuracy
 - Verifying percent recovery calculations for spiked samples.
 - c. Precision
 - Examining replicate samples for scatter.
 - d. Completeness
 - Computing the fraction of measurement data that remain valid after discarding any invalid data due to field or laboratory QC rejection.
 - e. Comparability
 - Identifying pertinent data characteristics which may limit comparability to other data sets.

Data which do not meet QC targets will be identified. These data will be reviewed further and a decision will be made as to their usability for the purposes of meeting objectives of this assessment.

11.0 DATA VALIDATION

Data quality and usability depend on many factors, including sampling methods, sample preparation, analytical methods, quality control and documentation. Precision, accuracy, representativeness, completeness and comparability of data will be evaluated at the end of each resource investigation. The determination of data usability will be made after following the data validation phase.

The following information will be reviewed in assessing data validity, as appropriate to individual studies.

Sample Collection and Preparation

1. Sampling date and time
2. Sampling team; observation taker and recorder, field team leader
3. Sampling location
4. Physical description of sampling location
5. Sample depth increment for soils
6. Sample collection techniques
7. Field preparation techniques (e.g., sieving, compositing, etc.)
8. Sample preservation technique(s)
9. Sample shipping data and laboratory analysis data
10. Laboratory preparation techniques (i.e., grinding, digestion)
11. Laboratory analysis methods
12. Laboratory analysis detection limits (either by specific notation or through reference method)

Laboratory QC

1. Laboratory/field instrumentation, calibration, standardization, and methods
 2. Proper sample bottle preparation
 3. Verification of standards using acceptable reference materials
 4. Analysis of laboratory (reagent) blanks
 5. Analysis of laboratory spikes if the analyte is amenable to spiking
 6. Analysis of field replicates (duplicates or splits) for each matrix
 7. Analysis of laboratory replicates (duplicates or splits)
 8. Presentation of tabulated QC data or QC charts/acceptance criteria
 9. QC limits consistent with QAPP targets
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Custody and Document Control

1. Field custody noted in field log book and transfer-of-custody documentation available
2. Samples hand delivered to laboratory and transfer-of-custody documentation available
3. Laboratory custody documented by transfer-of-custody documentation from either field personnel or shipper
4. Laboratory custody documented through designated laboratory sample custodian with secured sample storage area
5. Sample designation number(s) traceable through entire monitoring system
6. Field notebooks and all custody documents stored in secure repository or under the control of a document custodian
7. All forms filled out completely in indelible ink without alterations except as crossed-out (not erased) and initialed
8. Identity of sample collector

Sample Representativeness

1. Compatibility between field and laboratory measurements or suitable explanation of discrepancy
2. Analysis within time limits suitable for the preservation and analysis methods used
3. Sample storage within suitable temperature, light and moisture conditions
4. Proper sample containers
5. Proper sample collection equipment
6. Sample site selection criteria provide representativeness

The following items may be used to evaluate data:

- Holding time violation,
 - Interference problems or ICP serial dilution,
 - Exceedance of ICP interference check sample,
 - Exceedance of duplicate control limits,
 - Matrix spike recoveries outside control limits,
 - Instrument calibration problems,
 - Laboratory control standard outside control limits,
 - Blank contamination problems,
 - MSA correlation coefficient problems, and
 - GFAA analytical spike recovery or duplicate injection problems.
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There are no control limits or corrective actions for field QC statistics. Therefore, except in cases of gross errors, poor performance on field QC samples will not result in invalidating data.

12.0 QUALITY ASSURANCE PERFORMANCE AND SYSTEM AUDITS

12.1 LABORATORY PERFORMANCE

An audit may be conducted during the time that sample analysis is being conducted for projects undertaken for this damage assessment. These audits will verify each laboratory's ability to meet QA/QC requirements detailed in the research protocols or in this QAPP. An audit performed under another U.S. EPA or State of Montana-approved program may substitute for the NRDP audit.

12.2 PREVENTIVE MAINTENANCE

Preventive maintenance tasks and schedules recommended by manufacturers of analytical instruments and sampling equipment will be followed. Documentation of scheduled maintenance, routine repairs, and major overhauls will be maintained in instrument and equipment logbooks.

13.0 DATABASE MANAGEMENT

All analytical and QC data may be submitted in ASCII or dBase format, as appropriate. The ASCII or dBase format will assure that data are not handled or typed more than once. In addition, a hardcopy of electronically stored data will be compared to the stored data to verify its accuracy.